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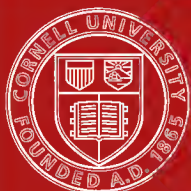
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**An introduction to general thermodynamic**



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AN INTRODUCTION  
TO  
General Thermodynamics

AN ELEMENTARY TREATISE ON THE  
FUNDAMENTAL PRINCIPLES AND  
THEIR SIMPLER APPLICATIONS

BY

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*FIRST THOUSAND*

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By HENRY A. PERKINS

## PREFACE

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THE writing of this book was originally undertaken as a result of a course of lectures given by the author, at Trinity College, on electro-chemistry and allied subjects, which seemed to demand a preliminary course of thermodynamics, where the general principles should be established, certain useful equations derived, and a few simple applications discussed, as a preparation to the real subject of the lectures. In looking over the field of textbooks in English treating of thermodynamics, in a broad spirit, without especial concentration on the steam-engine, it was a surprise to find none of recent date that could be said to do this in a form simple enough for the average undergraduate. The admirable treatises of Planck and Bryan are written for more advanced students, and could hardly be placed in the hands of those whose knowledge of heat does not extend beyond a general course in physics, and who have but the elementary notions of the calculus. It is for such students that this book is written; those whose training goes about as far as that of the audience Maxwell was addressing in his splendid treatise on heat. In fact that treatise was continually in my mind as I wrote, and I have attempted to put the subject before my readers in a similar spirit, but of course in more modern form, and with the aid of the elementary calculus, which Maxwell did not feel justified in using.

Thermodynamics will always be a difficult subject,

but for some time I have felt that it could be made easier by a treatment in which the mental unripeness of the undergraduate reader should be kept constantly in mind. A book written in such a spirit must follow certain general principles which will be admitted, I think, by every one who has taught the science. For instance, steps in the logical development of an equation or proof should not be omitted, however obvious they may seem to the author. The language used should be as clear and vivid as possible. Concrete illustrations should be largely employed in explaining such inherently difficult conceptions as entropy. Philosophic discussions of a purely theoretical interest, and a multiplicity of equations and symbols, introduced for the sake of absolute generality or mathematical rigor, should be either left out altogether, or only hinted at, as a preparation for a more advanced study of the same ground. Finally, from cover to cover, the text should follow an obvious sequence of ideas arranged along a central thread easily to be seen by the student; so that the various topics discussed should not seem like a disconnected exhibition of mathematical gymnastics, but a logical development of a marvellously systematic science.

In this brief treatise, I have attempted to follow these principles; and further have made no attempt to evolve peculiar or strikingly original methods of presentation; no unusual notation or phraseology has been adopted, and the traditional method of treatment has been followed, whenever it did not seem antiquated or unnecessarily obscure. It is possible that the elimination of the more purely philosophic side of the subject may have left the book a little pedantic and dry; while the



repeated explanation of what will seem to many, obvious steps, may produce an effect of monotony. I hope, however, that these drawbacks will be found justified by increased simplicity, clearness, and directness at which I have constantly aimed. If the attempt has been successful, such a book ought to be of use in preparing a class for a more profound study of thermodynamics from an author like Gibbs. It ought also to be useful as an introduction to all branches of physical chemistry, which can hardly be taught to-day without at least an introduction to thermodynamics. And, thirdly, it could be used, I hope, to advantage, as a short preliminary course, before plunging the technical student into one of the massive treatises on the steam-engine. If used in this way, some portions, such as the paragraphs on the gas thermometer, phase rule, etc., could be omitted to gain time, but even when thus abridged, I believe the book would result in giving the student a firmer grasp of the subject he is to specialize in, because of the wider outlook with which he would face the problems of his profession.

In conclusion I wish to express my grateful appreciation to Professor Lynde P. Wheeler of Yale University for his friendly assistance. His acute criticisms and scholarly suggestions have been of the greatest value to me in the preparation of this book.

TRINITY COLLEGE, HARTFORD,  
*November 2, 1911.*



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# NOTATION

The following table contains the most important symbols used in this book, with references to the page where each is first defined, and the parallel notation of Peabody, Bryan, Gibbs, and Planck.

Symbol	Name	Reference (page)	Peabody	Bryan	Gibbs	Planck
$p$	Pressure.....	3	$p$	$p$	$p$	$p$
$V, v$	Total volume, specific volume.....	3	$v$	$V, v$	$v$	$V, v$
$Q, q$	Quantity of heat.....	3	$Q$	$Q, q$	$H, Q$	$Q, q$
$T$	Absolute temperature.....	3	$T$	$T$	$t$	$\theta$
$t$	Temperature on Centigrade scale.....	3	$t$	$t$		$t$
$\eta$	Heat of compression at constant volume	6	$n$	$N$		
$\lambda$	Heat of compression at constant pressure.....	6	$o$	$M$		
$C$	Specific heat at constant pressure.....	6	$cp$	$\gamma p$	$s$	$cp$
$c$	Specific heat at constant volume.....	6	$cv$	$\gamma v$	$c$	$cv$

## NOTATION—Continued.

Symbol	Name	Reference (page)	Peabody	Bryan	Gibbs	Planck
$h$	Latent heat of change of pressure.....	6	$m$	$l_p$		
$l$	Latent heat of change of volume.....	6	$l$	$l_v$		
$\alpha_v$	Coefficient of dilatation at constant volume.....	11	$\alpha$			
$\alpha_p$	Coefficient of dilatation at constant pressure.....	11	$\alpha$	$\alpha_p$		
$E_T$	Isothermal modulus of elasticity .....	11		$\epsilon_T$	$e$	
$E_s$	Adiabatic modulus of elasticity.....	11		$\epsilon_s$	$e$	
$\gamma_T, \gamma$	Isothermal compressibility .....	12				
$\gamma_s$	Adiabatic compressibility .....	12				
$\kappa$	Ratio of specific heats.....	13 and 83	$\kappa$	$\kappa$		$\gamma$
$J$	Joule's equivalent .....	19	$J$	$J$		$J$
$U, u$	Intrinsic energy.....	20	$E$	$U, u$	$\epsilon$	$U, u$
$W, w$	External work.....	20	$W$	$W, w$		$-W$
$E$	Efficiency.....	34				

NOTATION—Continued.

Symbol	Name	Reference (page)	Peabody	Bryan	Gibbs	Planck
$S, s$	Entropy.....	42	$\phi$	$S, s$	$\eta$	$\Phi, \phi$
$F_{sv}, f_{sv}$	Thermodynamic potential.....	56			$\epsilon$	
$FT_v, fT_v$ $F, f$	Thermodynamic potential..... (at given volume)	56		$\mathfrak{F}_V \mathfrak{f}_v$	$\psi$	$F$
$FT_p, fT_p$ $F', f'$	Thermodynamic potential..... (at given pressure)	56		$\mathfrak{F}_p \mathfrak{f}_p$	$\xi$	$\Psi\theta$
$F_{sp}, f_{sp}$	Thermodynamic potential.....	56		$\mathfrak{F}_s \mathfrak{f}_s$	$\chi$	
$AT_p$	Available energy.....	60		$A$		
$AT_v$	Available energy.....	61		$A$		
$Asp$	Available energy.....	61		$A$		
$A_{sv}$	Available energy.....	61		$A$		
$L$	Latent heat of change of state.....	65	$\gamma$	$\lambda$		$L$
$R$	Perfect gas constant.....	77	$R$	$B$	$a$	$C, R$
$A$	Reciprocal of Joule's equivalent .....	78	$A$			

## NOTATION—Continued.

Symbol	Name	Reference (page)	Peabody	Bryan	Gibbs	Planck
$K$	Constant of adiabatic expansion.....	83				
$\pi$	Molecular pressure in general equation of state..... (also usual significance)	102				
$\phi$	Covolume in general equation of state...	102				
$a$	Van der Waals' pressure constant.....	103		$a$		$a$
$b$	Van der Waals' covolume.....	103		$b$		$b$
$v_c$	Critical volume.....	108		$v_c$		
$T_c$	Critical temperature .....	108		$T_c$		
$p_c$	Critical pressure.....	108		$p_c$		
$D$	Clausius' pressure constant.....	116		$C$		
$B$	Clausius' pressure constant.....	116		$B$		
$\epsilon$	Clausius' covolume.....	116		$a$		
$X$	"Cooling effect" in porous plug experi- ment.....	128		$\chi$		

## NOTATION—Continued.

Symbol	Name	Reference (page)	Peabody	Bryan	Gibbs	Planck
$\mu$	Chemical potential.....	133		$\mu$	$\mu$	
$H$	"Total heat" of saturated steam.....	147	$\lambda$			
$x$	Dryness, or "quality" of saturated steam.....	148 & 153	$x$	$x$		
$c'$	Specific heat of saturated vapor.....	148	$h$	$\gamma''$		$h$
$v'$	Specific volume of liquid state.....	149	$\sigma$	$v'$		
$v''$	Specific volume of saturated vapor .....	149	$s$	$v''$		
$\mu$	Exponent of adiabatic expansion of saturated steam.....	161	$\eta$			
$\rho$	"Internal heat" of vaporization ..... (also used for density)	163	$\rho$			





# AN INTRODUCTION TO GENERAL THERMODYNAMICS

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## CHAPTER I

### GENERAL HEAT RELATIONS

**Definition of the Subject.**—Thermodynamics is the science of heat regarded as a form of energy, and its relation to all other forms whether mechanical, chemical, or electrical. It embraces transformations that involve the production, destruction, or transfer of heat, as well as the mechanism by which that transfer is effected. Thus the theories of solutions, thermoelectricity, electrochemistry, radiation, conduction, and convection all come within its scope, although they are not always treated from the thermodynamic standpoint.

**Other Definitions.**—Certain terms are of such frequent use in thermodynamics that it will be well at once to define the most important before proceeding to discuss the fundamental laws of the science.

*Heat* is a property of a body known only by its effects. These may be perceived directly by the senses, as when we touch a hot body, and experience the sensation called heat; or indirectly, as when we see the mercury ascend

in a thermometer when the bulb is warmed. Heat is now known to be a form of energy due to the motion of the molecules of the heated body.

*Temperature* is the thermal state of a body which determines its relative hotness or coldness, and therefore, as will be seen later, determines the direction in which heat will flow between two bodies. It may be regarded as a measure, or consequence of the mean kinetic energy of the molecules that compose the body.

*Quantity of Heat.*—When a body absorbs heat without the performance of external work, either its temperature rises, or it changes its state of molecular aggregation, or both. The amount of such changes depends on the total quantity of heat added to the body. This quantity may be defined by aid of the rise of temperature when the body is not otherwise altered by the heat. The unit of quantity is the calorie, which is a quantity just sufficient to heat one gram of water from  $14.5^{\circ}$  C., to  $15.5^{\circ}$  C. This interval is chosen because it gives the same value to the calorie as the average quantity per degree between  $0^{\circ}$  and  $100^{\circ}$ . Quantity of heat may also be defined in terms of energy, or joules, as will be seen later.

*Change of State* is a transformation involving a rearrangement of the molecular structure of the body, as when ice melts, or water boils.

*An Isothermal Change* is one during which the temperature remains constant.

*An Adiabatic Change* is one during which no heat enters or leaves the body.

*Notation.*—Wherever such a distinction is significant we shall hereafter use the large letters to signify the

whole value of a certain quantity, and the small letters to signify its intensity or specific value. Thus  $p$  will denote force per unit area, or pressure;  $V$  will denote total volume,  $v$  volume per unit mass; referring to quantity of heat,  $Q$  will denote the total quantity and  $q$  the quantity per unit mass, etc.

As to the temperature it will be understood that  $T$  refers to absolute temperature on a scale having 100 degrees between the freezing and boiling points of water under standard atmospheric pressure;  $t$  (centigrade) refers also to an absolute scale (independent of the properties of any particular substance), but having a zero at the freezing point of water.

**Quantities that Determine a Body's Behavior.**—When we begin to examine the effect of heating a body, we notice certain obvious and immediate consequences of such heating, such as rise of temperature, change in volume, etc.; but bodies differ very much with regard to their behavior when heated, and we are thus led to a study of those quantities by which a body's thermal characteristics are determined. A preliminary investigation of such properties may be conducted without making any assumptions as to what heat is, or even postulating any laws as to its behavior. We need only discuss the conditions under which a body receives heat, and the immediate consequence of such heating as regards its external characteristics. This gives rise to the definition of three groups of coefficients, by which a body's behavior may be predicted. They are the calorimetric, thermometric, and thermoelastic coefficients. The first of these groups is concerned with a body's capacity for heat under various circum-

stances, the second with the effects produced in it by changes of temperature, and the third deals with its mechanical properties, such as elasticity, compressibility, etc., with or without transfer of heat.

**Quantities that Determine a Body's Condition.**—In order completely to define the state of a body, it is not enough to know its temperature. We must also know certain other quantities, as, for instance, the external pressure acting on its surface, its specific volume, internal energy, etc. Such quantities are clearly variable with the body's state, and are not characteristic coefficients like those discussed in the last paragraph. Now, in order that the relations between these defining variables may be handled without too great difficulty, it has been found necessary to limit the discussion to bodies whose states are completely defined by *three quantities*, and these three quantities must be so related that a determination of any two, which may be chosen as independent variables, enables us to calculate the third. This postulate fortunately is true of an immense number of actual bodies and systems of bodies, and conclusions based on this postulate are therefore true for all such cases.

But it must not be understood that even the majority of cases can be so easily described. The complicated states of living tissues doubtless need many determining quantities to describe them. As a fairly simple illustration of a body that is not completely defined by three variables, we may take an electrified soap-bubble which would only be completely determined if we knew the amount of the charge, the temperature, volume, and pres-

sure of the enclosed gas, and the surface tension of the soap mixture employed. Of these five variables, three are independent, and the remaining two obtained from the known laws of gases, surface tension, electrostatic repulsion, etc. In what follows, however, no such complicated cases will be discussed and we shall assume that the condition of a body may be completely defined by the three most important variables;  $p$ , the pressure,  $v$ , the specific volume, and  $t$ , the temperature. Moreover, since a knowledge of any two is sufficient to determine the third, we may regard these variables as interrelated by a function which is also supposed known, and whose exact form will be discussed farther on. For the present it will be sufficient to express it symbolically as

$$f(p, v, t) = 0 \quad . \quad . \quad . \quad (1)$$

These three variables are not the only three that might be used to describe a body's state. The total quantity of heat it contains could be chosen in place of one of them, and we shall later describe others that might be used with equal validity. However, the three mentioned above are the most fundamental, and will be largely employed in this discussion.

**Less than Three Variables.**—There are certain special cases where two or even one quantity may completely define a body's or system's condition. Dry saturated steam is wholly determined if we know its pressure and temperature, and, as these two quantities are connected by a relation obtained by experiment, we have only to know either one in order to find the other in the tables compiled from experimental data.

**"Heat Capacities."**—Since, in general, two of the

three variables must be known to define a body's state, the change effected in it when it is heated must be expressible in terms of two variables and two coefficients characteristic of the particular body examined. These coefficients come under the head of the calorimetric coefficients already discussed, and are known as heat capacities, or thermal capacities. We may thus state the perfectly general relation  $dQ = A da + B db$ , which expresses the effect of adding  $dQ$  joules of heat to the body whose calorimetric properties are defined by the coefficients  $A$  and  $B$ , and whose state is changed by infinitesimal increments of the variables  $a$  and  $b$ . Confining ourselves to the three variables already selected, three such equations, taking the variables two and two, are possible. They are:

$$dq = \eta dp + \lambda dv. \quad . \quad . \quad . \quad (2)$$

$$dq = C dt + h dp. \quad . \quad . \quad . \quad (3)$$

$$dq = c dt + l dv. \quad . \quad . \quad . \quad (4)$$

The coefficients  $\eta$ ,  $\lambda$ ,  $C$ ,  $h$ ,  $c$ ,  $l$  are the six capacities, and a large part of the business of thermodynamics is their determination in terms of measurable quantities, and a development of their relations to each other and to various other functions.

**Expansion of  $f(p, v, t)$ .**—The equation relating the three fundamental variables may be regarded as a fourth, in addition to the three just set down, and by its aid we may express any one of the six coefficients in terms of the others. To do this  $f(p, v, t) = 0$  is expanded as follows: The differential of any one variable of a function involving three, may be expressed in terms of the differentials of the other two thus:

$$\left. \begin{aligned} dp &= \frac{\delta p}{\delta t} dt + \frac{\delta p}{\delta v} dv \quad . \quad . \quad . \quad (a) \\ dv &= \frac{\delta v}{\delta t} dt + \frac{\delta v}{\delta p} dp \quad . \quad . \quad . \quad (b) \\ dt &= \frac{\delta t}{\delta p} dp + \frac{\delta t}{\delta v} dv \quad . \quad . \quad . \quad (c) \end{aligned} \right\} \quad (I)$$

where  $\frac{\delta p}{\delta t}$ , etc., are partial differential coefficients, assuming the third quantity constant. They might be written  $\left(\frac{dp}{dt}\right)_{v=\text{constant}}$  or simply  $\left(\frac{dp}{dt}\right)_v$ . The geometric meaning

of such equations is that when the body's condition is completely determined by three variables, its various states can be represented by points on a surface having the three variables as co-ordinate axes. It follows that the component of an infinitesimal motion on the surface parallel to any one axis may be taken in two steps each in a plane defined by that

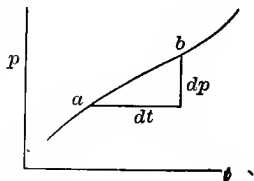


FIG. I.

axis and one of the other two. Thus on the  $p t$  plane where  $v$  is a constant, if we pass along the projection of the thermodynamic surface from  $a$  to  $b$ , the component of that motion in the direction of pressures is obviously given by  $\frac{\delta p}{\delta t} dt$ , while  $\frac{\delta p}{\delta v} dv$  expresses a similar step in the  $p v$  plane. The equations (a), (b), (c) are simply different expressions of the fundamental relation  $f(p, v, t) = 0$ ; thus there are only four available equations to determine six unknown coefficients; hence at least two of the thermal capacities must be known in order to solve for any one.

**Relations Between the Thermal Capacities.**—The solution proposed above is readily made. Taking equation (4), for example:

$$d q \doteq c d t + l d v;$$

substitute for  $d v$  from its expansion in (b), giving  $d q = c d t + l \left( \frac{\delta v}{\delta t} d t + \frac{\delta v}{\delta p} d p \right)$ , combining terms of the same variable,  $d q = \left( c + l \frac{\delta v}{\delta t} \right) d t + l \frac{\delta v}{\delta p} d p$ . But by equation (3),

$$d q = C d t + h d p.$$

Equating the coefficients of like variables, we have

$$C = c + l \frac{\delta v}{\delta t} \text{ and } h = l \frac{\delta v}{\delta p}.$$

The first of these is the more valuable relation, and five other similar ones may be obtained in exactly the same manner. These six equations are:

$$\lambda = l - \eta \frac{\delta p}{\delta v} \quad . \quad . \quad . \quad (5)$$

$$\eta = h - \lambda \frac{\delta v}{\delta p} \quad . \quad . \quad . \quad (6)$$

$$C = c - h \frac{\delta p}{\delta t} \quad . \quad . \quad . \quad (7)$$

$$h = \eta - C \frac{\delta t}{\delta p} \quad . \quad . \quad . \quad (8)$$

$$l = \lambda - c \frac{\delta t}{\delta v} \quad . \quad . \quad . \quad (9)$$

$$c = C - l \frac{\delta v}{\delta t} \quad . \quad . \quad . \quad (10)$$



In addition three other relations of the second type are obtainable, and are occasionally useful;

$$\eta = c \frac{\delta t}{\delta p} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

$$\lambda = C \frac{\delta t}{\delta v} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

$$h = l \frac{\delta v}{\delta p} \quad . \quad . \quad . \quad . \quad . \quad (13)$$

**Significance of the Capacities.**—In order to obtain a clearer idea of the exact significance of the thermal capacities, take equation (3) and suppose the heat  $dq$  is added while the pressure is kept constant; then  $dq = C dt$ , because  $dp = 0$ , or  $C = \left(\frac{dq}{dt}\right)_p$ , that is  $C$  is the rate at which a body absorbs heat per degree rise of temperature, at constant pressure. This is nothing but the familiar specific heat at constant pressure, so much used in the study of gases. Similarly  $c = \left(\frac{dq}{dt}\right)_v$ , or the specific heat at constant volume, while  $l = \left(\frac{dq}{dv}\right)_T$ , which is the specific heat per unit volume at constant temperature, and is thus closely connected to the “latent heat” of such processes as fusion, during which  $t$  remains constant. The other quantities, such as  $\eta = \left(\frac{dq}{dp}\right)_p$ , etc., have no familiar names, but are of great importance in the theory of thermodynamic transformations.

**Graphic Representation of the Thermal Capacities.**—This is effected by the use of isothermal and adiabatic lines on the pressure-volume diagram. An isothermal

line, as the name implies, represents the relation between the pressure and volume of a body while it undergoes a succession of changes at constant temperature. An adiabatic line represents a similar relation, but on the

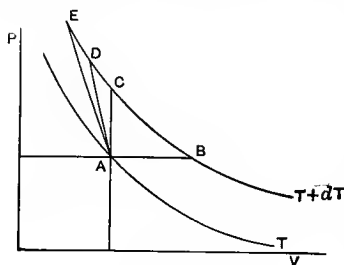


FIG. 2.

condition that no heat enters or leaves the body during the transformation.

Let  $T$  and  $T + dT$  be two isotherms infinitely close together. Let  $\overline{AD}$  be an adiabatic line; let  $\overline{AB}$  represent a line of constant pressure, and  $\overline{AC}$  one of constant volume, or an *isometric*.

The equation of the adiabat on the  $p v$  diagram is obtained by setting  $dq = 0$  in equation (2), then  $\eta dp + \lambda dv = 0$ . In going from  $A$  to  $B$ , as  $dp = 0$ , equation (3) becomes  $\left(\frac{dq}{dt}\right)_p = +C$ , which is the heat absorbed during this *isopiestic* transformation. In going from  $A$  to  $C$ ,  $\left(\frac{dq}{dt}\right)_v = +c$ , which is always smaller than  $C$ ; and from  $A$  to  $D$ , we have  $\left(\frac{dq}{dt}\right)_q = 0$ , since no heat is either absorbed or rejected. Thus as we pass from  $A$  to points farther and farther to the left, the specific heat  $\frac{dq}{dt}$  continually diminishes, and becomes zero when the adiabat  $AD$  is followed, but if we pass to a point  $E$  still farther to the left,  $\frac{dq}{dt}$  must become negative, which means that

heat is taken from the body during such a transformation. More useful expressions for  $\frac{dq}{dt}$ , and a discussion of the slope of both isothermals and adiabatics will be taken up farther on,—but enough has been said to give a fairly clear conception of the meaning and importance of the thermal capacities.

**Thermo-Elasticity.**—Instead of expressing a transformation with reference to the heat absorbed or rejected by the body or system of bodies, we may take account of the change in volume or pressure as the principal effects, thus giving rise to thermometric and thermo-elastic equations.

Let  $\alpha_v$  = the coefficient of dilatation of the substance at constant volume. At the pressure  $p$ , by definition

$$\alpha_v = \frac{1}{p} \left( \frac{dp}{dt} \right)_v$$

Let  $\alpha_p$  = the coefficient of dilatation at constant pressure. At the volume  $v$ , by definition,

$$\alpha_p = \frac{1}{v} \left( \frac{dv}{dt} \right)_p$$

Let  $E_T$  = the modulus of elasticity at constant temperature. By definition

$$E_T = -v \left( \frac{dp}{dv} \right)_T,$$

in which the minus sign indicates that increasing pressures are associated with decreasing volumes.

Let  $E_s$  = the modulus of elasticity when the change in volume takes place adiabatically. Then by definition

$$E_s = -v \left( \frac{dp}{dv} \right)_s$$

Further denote the reciprocal of  $E_T$  by  $\gamma_T$ , or simply by  $\gamma$ , then  $\gamma = \frac{1}{E_T}$ , and the reciprocal of  $E_s$  by  $\gamma_s$ , these quantities being the isothermal and adiabatic compressibilities respectively.

Now we have already seen that in general

$$\begin{aligned} dv &= \frac{\delta v}{\delta p} dp + \frac{\delta v}{\delta t} dt, \text{ dividing by } v \\ \frac{dv}{v} &= \frac{\delta v}{v \delta p} dp + \frac{\delta v}{v \delta t} dt, \text{ or} \\ \frac{dv}{v} &= -\gamma dp + \alpha_p dt. \quad . \quad . \quad . \quad (14) \end{aligned}$$

If  $v$  is constant, then  $-\gamma dp + \alpha_p dt = 0$ , hence

$$\left[ dt = \frac{\gamma}{\alpha_p} dp \right]_v \quad . \quad . \quad . \quad (15)$$

If  $p$  is constant, then  $\left[ \frac{dv}{v} = \alpha_p dt \right]_p$ , or

$$\left[ dt = \frac{dv}{\alpha_p v} \right]_p \quad . \quad . \quad . \quad (16)$$

But by definition  $\alpha_v = \frac{1}{p} \left( \frac{dp}{dt} \right)_v$ , hence combining with

(15) and remembering that  $\gamma = \frac{1}{E_T}$  we obtain

$$\alpha_v = \frac{\alpha_p E_T}{p} \quad . \quad . \quad . \quad (17)$$

Another valuable relation which connects  $E_s$  with  $E_T$  is derived as follows: When no heat enters or leaves the body,  $dq = 0$ , and equation (2) gives  $[\eta dp = -\lambda dv]_s$ ,

$$\text{or } \left( \frac{dp}{dv} \right)_s = -\frac{\lambda}{\eta}$$

$\therefore E_s = -v \left( \frac{d p}{d v} \right)_s = \frac{v \lambda}{\eta}$ , but by (11),  $\eta = c \left( \frac{d t}{d p} \right)_v$  and by (12),  $\lambda = C \left( \frac{d t}{d v} \right)_p$ . Further, from expansion (c) of equation (1), we have

$$d t = \left( \frac{d t}{d p} \right)_v d p + \left( \frac{d t}{d v} \right)_p d v$$

hence, at constant temperature

$$\left( \frac{d p}{d v} \right)_T = - \left( \frac{d t}{d v} \right)_p \left( \frac{d p}{d t} \right)_v.$$

Making these substitutions, we obtain

$$E_s = -v \frac{C}{c} \left( \frac{d p}{d v} \right)_T = \kappa E_T \quad . \quad . \quad (17')$$

when  $\kappa$  is the ratio of the specific heats.

**General Expression for Specific Heat.**—By the aid of the thermoelastic and thermometric coefficients we may obtain a general expression for  $d q / d t$ , the specific heat of any transformation whether at constant pressure, constant volume, or any other type. The transformation can be effected in two steps as has already been shown. Let the steps be chosen first at constant pressure, and second at constant volume, then

$$d q = C \delta t_1 + c \delta t_2 \quad . \quad . \quad . \quad (i)$$

But at constant pressure, by equation (16),  $\delta t_1 = \frac{\delta v}{v \alpha_p}$ , and

at constant volume, from (15),  $\delta t_2 = \frac{\gamma}{\alpha_p} \delta p$ , hence, substituting in (i),

$$d q = C \frac{\delta v}{\alpha_p v} + c \gamma \frac{\delta p}{\alpha_p} \quad . \quad . \quad . \quad (18)$$

But the total differential is equal to the sum of the two partial differentials or  $d t = \delta t_1 + \delta t_2$ , hence

$$d t = \frac{\delta v}{\alpha_p v} + \gamma \frac{\delta p}{\alpha_p}$$

thus giving the specific heat

$$\frac{d q}{d t} = \frac{C \frac{\delta v}{\alpha_p v} + \frac{c \gamma \delta p}{\alpha_p}}{\frac{\delta v}{\alpha_p v} + \gamma \frac{\delta p}{\alpha_p}} = \frac{\frac{C}{\alpha_p v} + \frac{c \gamma}{\alpha_p} \frac{\delta p}{\delta v}}{\frac{1}{\alpha_p v} + \frac{\gamma}{\alpha_p} \frac{\delta p}{\delta v}} \quad (19)$$

This is a homogeneous function in  $\delta p / \delta v$  and can always be solved if the various coefficients are known.

Other general equations for the specific heats like (18) can also be obtained as follows: taking equation (3) or  $d q = C d t + h d p$ , substitute the value of  $h$  obtained from (7), and divide by  $d t$ , giving

$$\frac{d q}{d t} = C - (C - c) \frac{\delta t}{\delta p} \frac{d p}{d t}$$

but from (15)  $\frac{\delta t}{\delta p} = \frac{\gamma}{\alpha_p}$  hence

$$\frac{d q}{d t} = C - (C - c) \frac{\gamma}{\alpha_p} \frac{d p}{d t} \quad . \quad . \quad . \quad (20)$$

Similarly starting with (4) it is easy to derive

$$\frac{d q}{d t} = c + (C - c) \frac{\delta t}{\delta v} \frac{d v}{d t}$$

and this reduces to

$$\frac{d q}{d t} = c + (C - c) \frac{d v}{v \alpha_p d t} \quad . \quad . \quad . \quad (21)$$

**Slope of Adiabatics.**—By the aid of the thermoelastic equation (18) we may examine the relative steepness of

isothermals and adiabatics on the  $p v$  diagram. Thus:

$$d q = C \frac{d v}{\alpha_p v} + \frac{c \gamma}{\alpha_p} d p$$

but if the curve is an adiabatic,  $d q = 0$  and

$$C \frac{d v}{\alpha_p v} = - \frac{c \gamma}{\alpha_p} d p, \text{ hence } \frac{d p}{d v} = - \frac{C E_T}{v c}$$

which is the tangent to an adiabatic at any point determined by  $v$ . Since there is one such tangent for each value of  $v$ , it follows that a line of constant pressures must cut an infinite number of adiabatics, none of which can intersect. When  $C$ ,  $c$ , and  $\gamma$  are all positive,  $d p/d v$  is negative, and the curve is like the adiabatic  $A D$  in Fig. 2.

As has already been pointed out, if we move from one adiabatic toward another higher in the series, as from  $A$  to any other

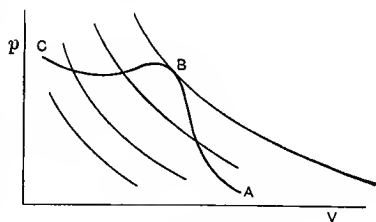


FIG. 3.

point to the right of  $D$ , heat must be added, but, descending the scale of adiabatics, heat must be withdrawn to effect the transformation. Thus if the  $p v$  surface be mapped out in a series of adiabatic lines, we can tell at a glance whether any assigned path involves a gain or a loss of heat. For instance, if the system of similar curves in the figure (3) are adiabatics, then a body whose pressure and volume vary according to the curve  $A B C$  will be absorbing heat from  $A$  to  $B$ , and rejecting it from  $B$  to  $C$ .

**Slope of Isothermals.**—In this case take equation

(14),  $\frac{dv}{v} = -\gamma \frac{dp}{p} + \frac{\gamma}{\alpha_p} \frac{dt}{t}$ , by transposing,  $dt = \frac{\gamma}{\alpha_p} \frac{dp}{p} + \frac{dv}{\alpha_p v}$ , but  $dt = 0$  for an isothermal change, hence  $\left(\frac{dp}{dv}\right)_T$

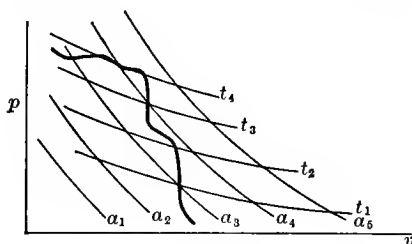


FIG. 4.

$$= -\frac{E_T}{v} \text{ which is}$$

the tangent to any isothermal for any value of  $v$ . Thus it is evident that the  $p$   $v$  diagram may also be mapped out in a system

of isothermals in an ascending scale of temperatures, none of which intersect, as was true also of the adiabatics.

**Comparison of Adiabatics and Isothermals.**—The ratio of the slope of the adiabatic to that of the isothermal for the same value of  $v$  is

$$-\frac{C E_T}{v c} \bigg/ -\frac{E_T}{v} = \frac{C}{c}.$$

But it is known that  $C > c$  both from experiment and theory, hence

$\frac{C}{c} > 1$ , which means

that the adiabatic lines are steeper than the isothermals. We may

now map out our plane with a net-

work of isothermals and adiabatics, and find by the course of any path whether a body is gaining or losing

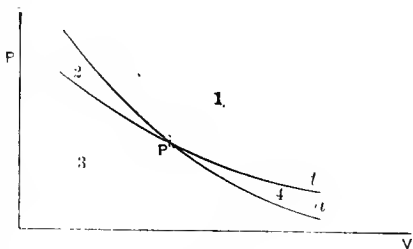


FIG. 5.



heat, or gaining or losing temperature, at any point along the transformation so represented. Thus in Fig. 4, the curves  $t$ ,  $t$ ,  $t$  are isothermals and  $a$ ,  $a$ ,  $a$  are adiabatics. A transformation that carries us from an isothermal toward one higher in the scale obviously means an increase of temperature, and if the slope of such a transformation is also greater than that of the adiabatic at the same point, there will be an absorption of heat at the same time. But if the curve representing the transformation has a slope between that of the isothermal and the steeper adiabatic, then the temperature is increasing while the body rejects heat. The various cases may be illustrated thus: starting from the point  $P$ , on Fig. 5, if we move into

the region 1,  $d q > 0$ ,  $d t > 0$

the region 2,  $d q < 0$ ,  $d t > 0$

the region 3,  $d q < 0$ ,  $d t < 0$

the region 4,  $d q > 0$ ,  $d t < 0$

## CHAPTER II

### THE FIRST AND SECOND LAWS OF THERMODYNAMICS

IN order to extend our field of inquiry to cover the relations between heat and work, it becomes necessary to make some assumptions concerning the nature of heat.

Without going into the long series of experiments that led up to the modern view, it will be sufficient to say that, as a consequence of the overwhelming mass of evidence, heat is now known to be a form of energy, and the first law of thermodynamics is a statement of this principle; or that heat and work are transformable into each other, and that when such a transformation takes place, *there is an exact proportionality between the energy of the kind that disappears, and the energy of the other kind that is produced at its expense.* It is really a special case of the law of the conservation of energy which states that the total amount of energy in the universe is constant, and that it is only possible to effect *transformations* between the various forms in which that energy may exist. The first law, however, really goes further, for we know from the data that proved this law, that mechanical work can be *entirely* converted into heat. As to *how much* heat can be converted into work, we are unable to say from data offered as evidence of the truth of the first law, which only affirms that when such a transformation does take place the proportionality still holds true.

**Joule's Equivalent.**—The numerical constant connecting heat energy as expressed in calories, and mechanical energy as expressed in joules, is known as "Joule's Equivalent," although it has been much more accurately measured since Joule's classic determination in 1843. Possibly the most accurate of recent determinations is that of Reynolds and Moorby, 1898, giving 4.1845 as the value of this constant, to be designated by the letter  $J$ . Taking account of various other observers, however, 4.185 is considered a better value. The meaning of this quantity is that one calorie of heat is equivalent to 4.185 joules of mechanical energy. Thus if  $Q$  units of heat are converted into work, we may write  $J Q = W$ , where  $Q$  is expressed in calories,  $W$  in joules, and  $J$  is the constant of proportionality, or Joule's equivalent.

**Suppression of  $J$ .**—In what follows  $J$  will not always be introduced in the analytic development of thermodynamic relations; for, being merely a numerical constant of zero dimensions, it is readily reduced to unity by a suitable choice of either of the systems of units. Therefore if heat is measured in joules instead of calories,  $J = 1$ , and the first law of thermodynamics may be written  $Q = W$  instead of  $J Q = W$ , where  $Q$  is measured in calories. It is only when one wishes to make numerical computations that it is necessary to express heat in calories. This is because the experimental values of the calorimetric constants are all referred to the calorie as the unit of heat, rather than to the joule; but in any equation it is easy to distinguish between such terms, and those that are measured in units of work, and they are readily reduced to a common scale by properly introducing  $J$  into the equation.

**Intrinsic Energy.**—According to the first law, when heat is converted into work, the work done is proportional to the heat that disappears in doing it. This does not mean, however, that all the heat supplied to a body can be converted into work; in fact this is never the case, and a portion of the heat supplied is concerned with raising the temperature of the body, or changing its molecular structure, or both. The changes thus produced in a body which do not result in external work are said to change its *intrinsic energy*. Intrinsic energy, therefore, is the energy a body contains by virtue of its temperature and molecular structure, or the sum of its internal kinetic and potential energies. This quantity will be denoted by  $U$  and  $u$ , according to whether the whole body is meant, or only a gram mass.

Whenever heat is supplied to a body the preceding principle is expressed by the perfectly general and fundamental equation,

$$dQ = dW + dU \quad . \quad (22)$$

or the heat added is equal to the sum of external work done and the change in intrinsic energy.

The sign of  $dQ$  is positive when the body or system considered receives heat;  $dW$  is positive when the system performs external work, and is negative when work is done upon it;  $dU$  is positive when there is a gain in intrinsic energy.

**Special Cases.**—This equation has three special cases.

(a) When the final state of the body is the same as its initial state. Then  $dQ = dW$ , which means that all the heat has been converted into work—a result impossible in practice.

(b) When no external work is done, as, for instance, when a body is heated in a vacuum. Then  $dQ = dU$ , and all the heat appears as intrinsic energy.

(c) The third case is when no heat is supplied at all, or  $dU = -dW$ , which occurs when work is done at the expense of the intrinsic energy; or, in case the transformation is in the opposite sense, all the work is converted into heat (or equivalent molecular change), as when a body is heated by friction. In this latter sense case (c) states the first law of thermodynamics in its most obvious form, as determined directly from experiment.

**Hydrostatic Pressure.**—In equation (22) the work  $dW$  may be done against any kind of opposing force, but there is a case of particular interest which arises when the work is done against a uniform pressure that acts normally to the expanding surface. In this special case  $dW = p dV$ , where  $p$  is the force exerted per unit area, and  $dV$  is the change in volume of the expanding body. Generally we shall write  $dw = p dv$ , when  $v$  is the specific volume. This special case is so common in the discussion of the principles of thermodynamics, that, unless otherwise stated, it will be assumed that the body under discussion is subjected to a uniform normal pressure. Since a pressure so defined is the kind considered in hydrostatics, the specification may be shortened to simply “hydrostatic pressure.”

**Exact Differentials.**—This assumption as to the pressure results in a most important simplification of many calculations, but even so, when  $dw = p dv$ , the expression can only be integrated if we know the relation between  $p$  and  $v$  during the particular expansion con-

sidered. In other words we must know the path followed in order to evaluate the integral  $\int_{v_1}^{v_2} p \, dv$ ; hence  $d w$  is not an exact differential.

However,  $d U$  (and, of course,  $d u$ ) is an exact differential, because the intrinsic energy of a body depends on its molecular condition only, and is independent of the manner in which that energy was gained, hence, if we know the intrinsic energy corresponding to two different states of the same body, their arithmetical difference is the energy gained regardless of the path followed; *i.e.*,  $\int d U = U_2 - U_1$  which is the property of an exact differential. But since  $d U$  is exact, while  $d W$  is not,  $d Q$  cannot be exact either, as is readily seen from equation (22).

**Special Case.**—There is, however, one special case in which  $d Q$  may become an exact differential. This is when  $d W = 0$ , or a process during which no external work is done. Then  $d Q = d U$ , and it must then be exact since  $d U$  is so always.

**Closed Cycles.**—If we perform a closed cycle of operations on any body; that is, bring it back to its initial state, then  $\int d U = 0$  taken around the cycle; hence  $\int d Q = \int d W$ . This equation indicates that any closed cycle of operations may serve as a means to

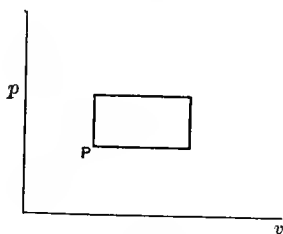


FIG. 6.

evaluate  $J$  provided  $\int d w = J \int d q$  can be measured over the cycle. Certain simple cycles may be used as

an illustration of this principle, and as a means of deriving several useful equations. For instance, suppose we start at the point  $P$  and perform an infinitesimal rectangular cycle in a clockwise direction. Then, in general  $d q = \eta d p + \lambda d v$  where  $\eta$  and  $\lambda$  are the capacities at the point  $P$ . Hence, during the first step, at constant volume,

$$d q_1 = \eta d p$$

during the second step, at constant pressure,

$$d q_2 = \left( \lambda + \frac{\delta \lambda}{\delta p} d p \right) d v$$

during the third, at constant volume,

$$d q_3 = - \left( \eta + \frac{\delta \eta}{\delta v} d v \right) d p$$

and during the fourth, at constant pressure,

$$d q_4 = - \lambda d v$$

In addition, we have

$$d w = d p d v = J d q$$

Summing up over the cycle,

$$\Sigma d q = \left( \frac{\delta \lambda}{\delta p} - \frac{\delta \eta}{\delta v} \right) d p d v$$

or

$$J \left( \frac{\delta \lambda}{\delta p} - \frac{\delta \eta}{\delta v} \right) = 1 \quad . \quad . \quad . \quad (23)$$

from which  $J$  could be calculated if the partial derivatives are known.

A similar process may be pursued, using a cycle bounded by isothermals and lines of constant volume. In this case, any change in  $q$  is given by  $d q = c d t +$

$l dv$ , where either  $v$  or  $t$  is constant. The four infinitesimal changes are:

at constant volume  $d q_1 = c dt$

at constant temperature  $d q_2 = \left( l + \frac{\delta l}{\delta t} dt \right) dv$

at constant volume  $d q_3 = - \left( c + \frac{\delta c}{\delta v} dv \right) dt$

at constant temperature  $d q_4 = - l dv$

therefore  $\Sigma d q = \left( \frac{\delta l}{\delta t} - \frac{\delta c}{\delta v} \right) dv dt$ .

But the area of the cycle is given by  $dv \frac{\delta p}{\delta t} dt = dw =$

$J dq$ , hence  $J \left( \frac{\delta l}{\delta t} - \frac{\delta c}{\delta v} \right) dv dt = dv \frac{\delta p}{\delta t} dt$ , or

$$J \left( \frac{\delta l}{\delta t} - \frac{\delta c}{\delta v} \right) = \frac{\delta p}{\delta t} \quad . \quad . \quad . \quad (24)$$

A third case is when the cycle is bounded by isothermals and lines of equal pressure, which, by an exactly similar process, yields

$$J \left( \frac{\delta h}{\delta t} - \frac{\delta C}{\delta p} \right) = - \frac{\delta v}{\delta t} \quad . \quad . \quad . \quad (25)$$

**Graphic Representation of U, Q, and W.**—The integrals of the change of intrinsic energy, the heat absorbed (or rejected), and the work done during any transformation can be represented graphically, as Rankine has shown, in the following manner:

Suppose we carry a body from  $A$  to  $B$  following any path. The external work  $\int_A^B dW$  is clearly given by the area  $ABba$  which is the integral of  $p dv$  over the path  $AB$ . The total intrinsic energy at  $A$  is represented by the area enclosed between an adiabatic  $A\alpha$  produced



until it touches the  $v$  axis, and the axis itself; because if such a body expanded adiabatically until the pressure were zero, it would have expended all its intrinsic energy in external work, and no more work would be possible at a point where  $p = 0$ . Similarly the total intrinsic energy at  $B$  is represented by the total area between the

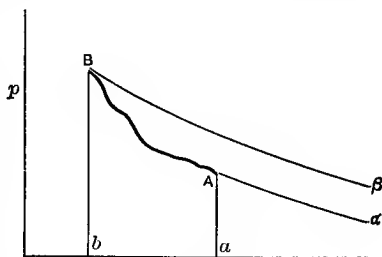


FIG. 7.

adiabatic  $B\beta$  and the  $v$  axis; hence the gain in intrinsic energy in passing from  $A$  to  $B$  is  $\int_A^B dU = U_B - U_A$  and is represented by the area  $\beta B b a A \alpha$ . Thus, because, as we moved from  $A$  to  $B$ , there has been a gain in the intrinsic energy,  $dU$  is positive. Also, since we moved from large to smaller volumes, and from low to higher pressures, it is evident that the body was compressed; hence  $dW$  is negative. Finally  $\int dQ = + \int dW + \int dU = \text{area } A B \beta \alpha$ , which means that heat was added to the body simultaneously with the compression, and both causes united to increase the intrinsic energy.

If the direction had been from  $B$  to  $A$  it would mean that positive work proportional to  $b B A a$  had been done at the expense of intrinsic energy, and heat, proportional to  $\alpha A B \beta$  had been taken from the body. Similarly we might study the case when  $AB$  slopes the other way (see Fig. 8). Now, in passing from  $A$  to  $B$ , positive work would be done by the body by virtue

of its expansion against an increasing pressure. There would also be a gain in intrinsic energy, and heat would have to be added to the body. Or, if we go from  $B$  to  $A$ , all these three quantities would be negative. The

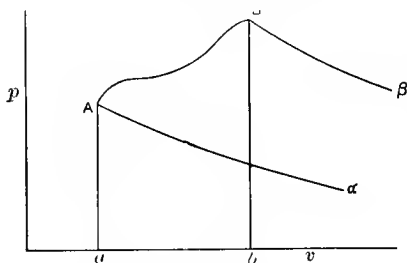


FIG. 8.

representation by areas in this case, however, is not so clear owing to their overlapping.

**Summary.** — We have so far made but two assumptions that are not inherent in all mathematical

discussions; the fundamental assumption of the conservation of energy, and, the assumption that the state of the body is completely defined by three quantities of which two are independent variables. So far we have chosen  $p$ ,  $V$  and  $t$  as these quantities. This was, however, not necessary. We might have chosen  $p$ ,  $V$  and  $U$  instead, and  $t$  could have been represented as an area, just as we have represented  $U$ . In the succeeding chapters other quantities will be defined that may also be taken as independent variables.

## THE SECOND LAW OF THERMODYNAMICS

We have already seen that the First Law of Thermodynamics says nothing as to the amount of a given quantity of heat it is possible to convert into work. In order to arrive at a definite conclusion on this point, it will be necessary to make one more fundamental postu-

late with regard to heat. The Second Law of Thermodynamics (as this postulate is called) is concerned with the behavior rather than the nature of heat. It may be stated in a variety of ways, but the one that presents it most vividly to the mind, though not historically the first to be formulated, will be given here.

**Clausius' Statement.**—This clearest statement is due to Clausius who announced that—"It is impossible for a self-acting machine, unaided by any external agency, to convey heat from one body to another at a higher temperature." This might be paraphrased thus: heat cannot flow unaided from a colder to a hotter body, but it tends invariably to seek lower levels of temperature.

The second law rests on our experience for its verification, but, unlike the first, it cannot be said to be derived from direct experiment; however, its acceptance has never led to incorrect conclusions, it has always been verified indirectly by experiment, and we are therefore bound to consider it as proved, even if it cannot be rigorously established either by *a priori* reasoning or direct experiment. Boltzman and Gibbs, indeed, have shown as a result of statistical methods that such a generalization is legitimate, considering that we deal with matter in large aggregations of molecules. In the same way it would be legitimate to formulate vital statistics as laws, provided we are dealing with a community numbering many millions, but in a village of a few hundred inhabitants, we should not be justified in so doing. From Clausius' statement of the Second Law, we can derive it in another form, called "Carnot's Principle," although really Carnot preceded Clausius in his formulation of this principle; and in Carnot's

form we shall find an answer to the question as to the availability of heat for the performance of useful work. Before proceeding, however, to obtain Carnot's principle, it will be necessary to make some preliminary definitions, and describe "Carnot's Cycle."

**Reversible and Irreversible Processes.**—Whenever a certain succession of changes is made in the conditions that affect a body, that body will, in general, experience a corresponding succession of effects. Now, if the causal changes are reversed and produced in inverse order, and if the resulting effects are also followed through in inverse order, thus bringing the body back to the exact condition from which it started, by the same path retraced, then the process is said to be a reversible one. As an example of an approximately reversible process we may consider stretching a long helical spring, and then allowing it to return to its original form.

If, however, when we wish to return the body to its original condition, we are unable to do so by a succession of changes exactly similar to the original, the process is irreversible. An extreme case would be the explosion of a charge of gunpowder, when the resulting gases cannot be brought back to the original form at all. But there are many irreversible processes where the original state can be recovered, though by a different path. This is true of all actual approximations to reversible processes, for friction always enters in and destroys complete reversibility. For instance, in the case of the helical spring cited above, as a result of the stretching an imperfectly elastic body, a minute amount of heat will be developed and dissipated, which is not returned to the

wire when it recovers its original shape, hence the process is not exactly reversible.

**Reversible and Irreversible Cycles.**—Suppose, instead of simply carrying a body from one state to another by means of a certain series of changes, we carry it through a succession of changes until it is brought back to the starting point, without, necessarily, having retraced any of the steps. Such a series of events is called a cycle. The case of the helical spring is a cycle, but there are cycles also where no steps are retraced, and yet, at the end, the body is back where it started. A rotating wheel performs such a cycle once per revolution. The water used by a condensing engine performs such a cycle. It is first vaporized in the boiler, then expands in the cylinder, is condensed, and finally pumped back into the boiler again. Such a cycle may be represented by a closed curve in a suitable diagram, and for that reason is often spoken of as a closed cycle.

Cycles may be either *reversible* or *irreversible* according to whether they can be traced through in either sense. The case of the rotating body is strictly reversible if there is no friction. But, if friction is taken account of, some heat will have been produced during a rotation in one direction at the expense of mechanical work, and it is obvious that the work will not be recovered, with a consequent withdrawal of heat, if it is turned back in the other direction.

The case of water in a condensing engine is an even more striking case of an irreversible cycle. To consider only one of the steps, its perfect reversal would involve taking cold water from the boiler into the injector pump, which is impossible, because the process of heat-

ing the cold feed water by mixing it with the hot water already in the boiler is an essentially irreversible process.

We have, then, cycles which may be made almost perfectly reversible, and others that involve an irreversible transformation, and are, therefore, irreversible cycles.

**Carnot's Cycle.**—In proving his principle, Carnot made use of an imaginary engine, performing a particular cycle of operations, which has been named after him,

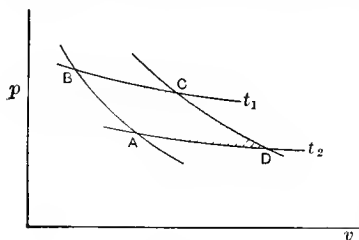


FIG. 9.

“the Carnot cycle.” It is by no means the only reversible cycle approximately obtainable in an engine—in fact there are others more readily obtained—but because of its simplicity it is usually chosen to illustrate

the ideal engine cycle. It consists in a contour made by two adiabatics and two isothermals as shown in Fig. 9, and can be nearly realized by a conceivable engine as follows. Imagine a substance which expands under the action of heat, and which may be compressed by mechanical pressure; in other words, almost any known substance. Suppose this substance  $S$  is contained in a cylinder, so that it can be compressed or expanded by moving a piston in or out. At the beginning let  $A$ , on the diagram, indicate its state. Now let it be compressed in such a way that the heat evolved by compression is not allowed to escape, either by radiation or conduction, until it reaches any other state,  $B$ , whose temperature  $t_1$  is greater than  $t_2$ , which was its original temperature. This is called an adiabatic compression. Next put it

in contact with a generator of heat,  $G$ , whose temperature is very slightly higher than that of the body. Heat will then flow into  $S$ , and, if the supply of heat is sufficiently great, the slight difference of temperature will be maintained while  $S$  is allowed to expand, as a result of this inflow of heat. Thus  $S$  follows the isothermal curve  $BC$  as far as we wish to continue the expansion.

Next remove  $S$ , and place it as before so that it cannot lose or gain heat. If left to itself, it will continue to expand while its temperature falls, and this is allowed to proceed until it reaches the original temperature  $t_2$ . Finally, to return it to its original state, it is put in contact with a refrigerator, or receiver of heat, at a temperature slightly colder than  $t_2$ , and the piston is forced down, thus raising the pressure and diminishing the volume while the heat of compression is removed without allowing the body to vary from the temperature  $t_2$ . It will be seen that it is necessary to suppose a slight difference of temperature between  $S$  and the generator during the isothermal expansion, and between  $S$  and the refrigerator during the isothermal compression, in order to allow for the flow of heat between the two bodies. This flow, as we have already pointed out, is irreversible, and Carnot's cycle is, therefore, strictly speaking not a reversible cycle, but theoretically it can be made as nearly reversible as we choose, by making the difference of temperature we have mentioned infinitesimal. This would greatly prolong the time required to go through the cycle, and it would become infinitely long when the two temperatures became equal. Thus perfect reversibility is the limiting case of a Carnot's cycle performed with diminishing temperature difference.

At the end of such a cycle, the body has regained its original state by a nearly reversible process; but three important external effects have resulted: a certain amount of heat has left the generator, another quantity has been absorbed by the refrigerator, and a certain net amount of mechanical work has been performed by the substance acting on the piston.

We can evaluate the work performed as follows. During the first, or adiabatic, compression an amount of work proportional to the area  $A a b B$  was done on

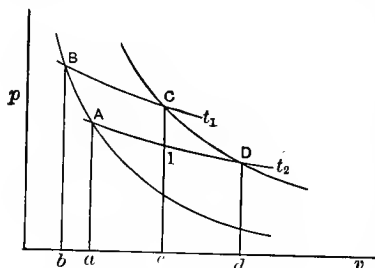


FIG. 10.

the substance by the external force acting on the piston. This we have agreed to call negative work. Next, while the substance expanded isothermally, it did work on the piston proportional to  $B C c b$ .

From  $C$  to  $D$  it did further positive work, proportional to  $C D d c$ , and finally when it was compressed isothermally negative work was done proportional to  $D d a A$ .

Thus we have, as the outstanding work accomplished, the positive area  $A B C D$  which is readily obtained by taking the algebraic sum:

$$\begin{array}{r}
 + b B C c \\
 + c C D d \\
 - a A D d \\
 - b B A a \\
 \hline
 + A B C D
 \end{array}$$



Hence the area enclosed between any two adiabatics and any two isothermals is proportional to the work done by the substance in following a Carnot cycle in the clockwise sense. If we had reversed the process, we should have obtained  $-A B C D$ , which would indicate that energy had been supplied from some external source to complete the cycle. This would also involve a reversal of the transfer of heat, and we should be withdrawing heat from the refrigerator and delivering heat to the generator, thus causing heat to flow from lower to higher temperatures, but at the expense of mechanical energy. In this connection Maxwell points out that there are two ways to transfer heat from hotter to colder bodies, *i.e.*, by an irreversible flow of conducted or radiated heat, and by a more or less reversible process involving the production of external work; but there is only one way by which the reverse may be accomplished, and that is by expending mechanical energy operating through a more or less reversible process.

It has just been shown that the area enclosed by Carnot's cycle represents the amount of mechanical work involved in the complete process. This is true of any closed cycle on the  $p v$  diagram, and the above conclusion is included in the following general proof which applies to any closed curve.

Suppose (Fig. 11) we pass from  $A$  to  $B$  by any path, then the work done is obviously  $\int_A^B p \, dv$ . Next pass from  $B$  to  $A$  by any other path as indicated, and we do work that is given by  $\int_B^A p \, dv$  integrated over the lower

path in the diagram. The difference is evidently equal to the enclosed area, and this is equal to the total area integral taken from  $A$  back to  $A$  again in the direction

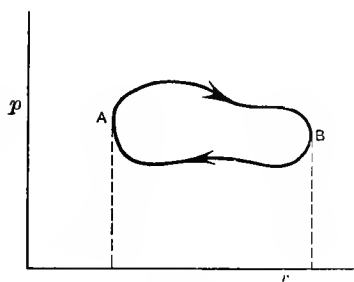


FIG. 11.

of the arrows; that is

$$\int_A^B p \, dv - \int_B^A p \, dv = \int_A^A p \, dv.$$

If the two paths coincide, the first two integrals are equal, and the work is zero.

### Carnot's Principle.

—We are now in a position to understand Carnot's principle and its proof. The principle is that the efficiency of an engine, operating in a reversible cycle between two given temperatures, is as great or greater than the efficiency of any other engine operating between the same two extremes of temperature. The proof is extremely simple, and depends really on the second law in its form as stated by Clausius.

Suppose that two engines,  $A$  and  $B$ , are operating between the same limits of temperature. Let  $A$  be a reversible engine having an efficiency  $E$ , and let  $B$  have an efficiency  $E'$  greater than  $E$ . Now let  $A$  be driven backward by  $B$  so that it takes heat from the refrigerator, and delivers it to the generator, and let  $B$  take just enough heat from the generator to develop exactly the work per cycle necessary to drive  $A$ . Then, if  $Q$  is the amount of heat delivered to the generator in each cycle by  $A$ , the work required to drive it must be  $Q E$ , while

the work done by  $B$  must equal  $Q' E'$ , where  $Q'$  is the quantity of heat it takes from the generator. But by hypothesis  $Q E = Q' E'$  and  $E' > E$ , hence  $Q > Q'$  which means a net gain of heat by the generator. Further let  $P$  = the amount of heat withdrawn from the refrigerator by  $A$ , and let  $P'$  = the amount of heat given to the refrigerator by  $B$ , then the work done on

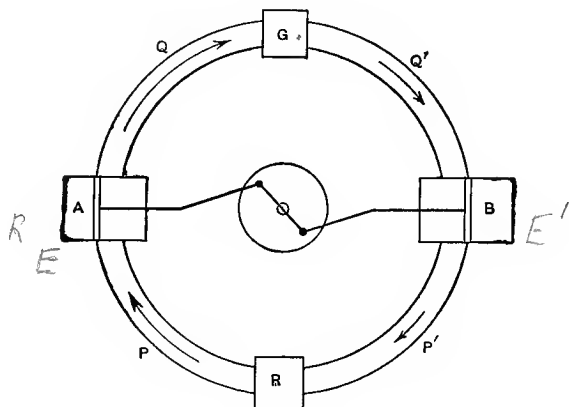


FIG. 12.

$A = Q - P$ , and the work done by  $B = Q' - P'$ , but these quantities are equal by hypothesis, or

$$Q - Q' = P - P'$$

and since  $Q > Q'$ , it follows that  $P > P'$ , which means a net loss of heat by the refrigerator.

This may be illustrated diagrammatically as shown in Fig. 12, where  $G$  is the generator,  $R$  the refrigerator,  $A$  and  $B$  are the engines both acting on the same crankshaft; and the arrows indicate the direction of the flow

of heat, and their lengths the relative magnitude of the quantities in motion. The conclusion just arrived at means that in this self-contained system, there is a steady flow of heat into the generator, accompanied by a steady withdrawal of heat from the refrigerator; but this is contrary to the principle already laid down in the second law (although the first law is not violated), and therefore  $B$  cannot be more efficient than  $A$ .

It is now possible to determine the efficiency of a reversible engine working between two temperature limits, and so obtain an algebraic expression of the second law applied to all cases where the heat is all taken on at one temperature, and rejected at another.

**Efficiency of a Reversible Cycle.**—In accordance with the proposition just proved, that all reversible engines operating between the same limits of temperature have the same efficiency, it is clear that the efficiency can depend only on the temperature of the generator (or refrigerator), and the interval between the two temperatures, and must be independent of the working substance, and the particular cycle employed. We are thus justified in writing  $E = f(t, \Delta t)$ .

Now Carnot supposed that the work done by an engine operating in a reversible cycle was due to the transfer of a quantity of heat,  $Q$ , from the higher temperature level  $t_1$  to the lower level  $t_2$ , just as a given mass of water, in passing from a higher level to a lower, does useful work in a water-motor at the expense of its potential energy, but remains the same as to the total mass. Carnot considered heat as an indestructible fluid that did work by virtue of its motion from one body to another. But at that time (1824) the law of

the conservation of energy was not understood, and particularly its truth as expressed in the first law of thermodynamics. It remained for Clausius to point out that, as heat is not a fluid, but a form of energy, a certain quantity of it must disappear when work is done, and, as we have seen, this ratio of the work done to the quantity that disappears must be constant for all such transformations of energy.

We can, therefore, write another expression for the efficiency based on the first law of thermodynamics, *i.e.*,

$E = \frac{Q_1 - Q_2}{Q_1}$  where  $Q_1$  is the amount of heat received

from the generator, and  $Q_2$  the amount delivered to the refrigerator. The numerator is, therefore, the amount of heat that disappears in the production of mechanical work, and is proportional to the output of the engine, and the denominator is the total heat delivered to the engine, and therefore proportional to the mechanical

energy input. This may be written  $E = \frac{\Delta Q}{Q} = f(t, \Delta t)$

$= f_1(t) \Delta t$ . The nature of the function  $f_1$  is not self-evident. It is called Carnot's function of the temperature. Carnot actually supposed it to be a constant, thus making the efficiency to depend only upon  $\Delta t$  and not upon the temperature of either the generator or refrigerator, as would, of course, be the case in the hydraulic analogy he followed; but this is the same as assuming that the amount of heat received is the same as that rejected, and thus contradicts the first law of thermodynamics. Therefore  $f_1$  must vary with the temperature and must depend for its form on the particular scale of temperature employed.

**Absolute Temperature Scale.**—This leads us to the definition of the absolute scale as proposed by Lord Kelvin. If we assume a scale whose zero is such that a Carnot engine having a refrigerator at that temperature would utilize all the energy supplied to it, it will have an efficiency of 100 per cent, and therefore any lower temperature would result in an efficiency higher than 100 per cent, which is absurd. Hence a zero so defined is the absolute zero.

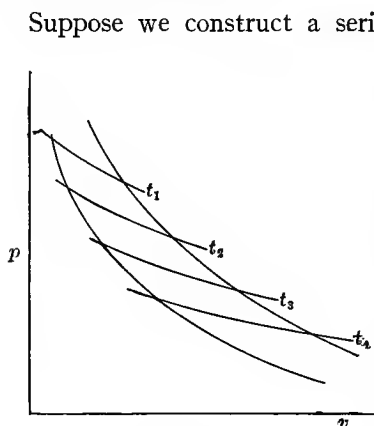


FIG. 13.

Suppose we construct a series of reversible engines each developing the same amount of work per cycle, and so arranged that each receives the heat rejected by the one next higher in the series. The diagram of such a system, supposing they use the Carnot cycle (which is, however, not necessary), would be a chain of

quadrilaterals enclosed between two adiabatic lines, and a series of isothermals as shown in Fig. 13. This series cannot go on indefinitely, because each engine consumes a portion of the original energy delivered to the first one, and if the energy consumed by each is  $q$ , and that supplied to the first is  $Q$ , there can be only  $Q/q$  such steps, at the end of which series we shall reach the absolute zero defined above. Now if we suppose the temperature of the generator supplying heat to the first engine to be

the temperature of melting ice, as determined for the zero of the centigrade scale, and take  $q$  such that  $Q/q = 273$ , then the isothermals of such a chain will each correspond to a degree of the absolute scale, and this series may be carried as far above  $0^\circ$  C. as we wish, always keeping  $q$  constant, or, what is the same thing, making the areas of all the quadrilaterals equal to each other.

This scale, as we shall see later, is the same as the absolute scale determined by a gas thermometer using an ideal gas, and it is closely approximated by the scale of the hydrogen thermometer. But Kelvin's definition of the absolute scale, as just explained, has the great advantage that it is expressed in terms of energy, and is independent of the properties of any particular substance, or any hypothesis concerning the exact nature of heat energy.

In all thermodynamic formulæ that involve the second law it is understood that the temperature is measured on the absolute scale. In many of the equations, however, the temperature enters only as a differential,  $dT$ , or as a difference  $T_1 - T_2$  or  $t_1 - t_2$ , and in these cases it is immaterial whether we write  $dT$  or  $dt$ , or  $T_1 - T_2$  or  $t_1 - t_2$ , since we have assumed both  $T$  and  $t$  to be measured in "absolute" degrees. In fact in all cases  $dt$  may be written for  $dT$ ; but when the integral temperature is considered, it must be remembered that  $T = t + 273$  approximately.

**Carnot's Function.**—Let us now assume that there are  $n$  steps in a chain of engines performing simple reversible cycles, and that the amount of heat delivered to the hottest is  $Q = qn$ . The amount delivered to the second will then be  $Q - q = q(n - 1)$ , and to the third  $Q - 2q$

$= q(n-2) \dots$  and to the  $n$ th  $Q - (n-1)q = q$ .  
 Thus the efficiency of the first is  $\frac{q}{qn} = \frac{1}{n}$ , and of the second,  $\frac{q}{q(n-1)} = \frac{1}{n-1}$ , and of the third,  $\frac{q}{q(n-2)} = \frac{1}{n-2}$ , and of the  $n$ th,  $\frac{q}{q} = 1$ , but since by the definition of the absolute scale  $n = T$ , the denominators of the efficiencies are precisely the temperatures of the sources of heat for each of the cycles considered; hence we may write that the efficiency of each of these unit engines is  $\frac{1}{T}$ , or  $E = \frac{q}{Q} = \frac{1}{T}$ , or if we consider the efficiency of a chain of  $m$  such engines,  $m q$  units of heat will be absorbed, and the output being  $m q$ , the collective efficiency of such a multiple system is  $E_m = \frac{mq}{Q} = \frac{m}{T}$ . But  $m$  also represents the difference of temperature in absolute degrees between the generator of the first engine of this series and the refrigerator of the last, hence we may write  $m = \Delta t$ ; but  $m q = \Delta Q$ , being the total quantity of heat absorbed by the  $m$  engines and converted into mechanical power. The expression of the efficiency then becomes  $E = \frac{\Delta Q}{Q} = \frac{\Delta T}{T}$  and comparing this with Carnot's equation of efficiency, *i.e.*,  $E = f_1(t) \Delta t$ , it is evident that  $f_1(t) = \frac{1}{T}$  if  $T$  is measured on the absolute scale.

**Efficiency of a Reversible Cycle.**—We can now obtain the efficiency of any engine operating in a simple reversible cycle between any two temperatures  $T_1$  and  $T_2$ , that absorbs  $Q_1$  units of heat entirely at the higher



temperature, and rejects  $Q_2$  units entirely at the lower. This expression is

$$E = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1} \quad . \quad . \quad . \quad (26)$$

which is thus the highest attainable efficiency between the two temperatures considered. The equation  $E = \frac{T_1 - T_2}{T_1}$  is really a statement of the second law of thermodynamics, as Carnot's principle was used in the fundamental assumption that the efficiency of a reversible engine depends only on the range of temperature between generator and refrigerator and the temperature of one of them.

This equation may be slightly modified into a form that will be found very useful. Taking  $\frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}$  it follows that  $\frac{Q_2}{Q_1} = \frac{T_2}{T_1}$ , or  $\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$ . That is, in any simple reversible cycle, the heat absorbed and the heat rejected are proportional to the temperatures of the generator and refrigerator respectively.

A point of practical interest is that if an engine is operating in the Carnot cycle, or any reversible cycle between two limiting temperatures, it is more advantageous, from the point of view of efficiency, to lower the temperature of the refrigerator by a certain number of degrees  $\epsilon$ , than to raise the temperature of the generator by the same amount, for  $\frac{(T_1 + \epsilon) - T_2}{T_1 + \epsilon} < \frac{(T_1 + \epsilon) - T_2}{T_1}$  but this latter fraction equals  $\frac{T_1 - (T_2 - \epsilon)}{T_1}$ , which is the efficiency when  $T_2$  is lowered by  $\epsilon$ .

## CHAPTER III

### ENTROPY

As has just been proved, whenever a quantity of heat  $Q$  is delivered to an ideal engine working in a reversible cycle, the amount of work that is obtained is  $Q E$  or  $\frac{Q (T_1 - T_2)}{T_1}$  which is the maximum of energy obtainable by any engine working between the same limits of temperature. The portion of  $Q$  which is thus available under ideal conditions as energy may be expanded as follows:

$$Q E = Q \frac{T_1}{T_1} - Q \frac{T_2}{T_1} = Q - \left( \frac{Q}{T_1} \right) T_2.$$

The second term of this expression is evidently the quantity of heat that is not convertible into useful mechanical work. This equation is simply a statement that the available energy of an engine is equal to the total energy supplied less the unavailable energy. This unavailable energy becomes zero only when the lowest temperature  $T_2$  is the zero of the absolute scale. At that point the available energy =  $Q$ , and  $E = 1$ . The quantity enclosed in the parenthesis  $\left( \frac{Q}{T_1} \right)$  when applied to a reversible process as we have assumed, is of such importance in the theory and practice of heat engines, that it has been given a particular name, *entropy*, and a symbol, which will be  $S$  in this book.

*Entropy, then, is that quantity which, multiplied by the lowest available temperature, gives the unavailable energy.*

When the  $Q$  units of heat are supplied to the engine, if  $T_2$  is regarded as fixed by some particular considerations at a minimum value, say the freezing point of water, then there is a certain amount of energy that is bound to be wasted. This waste is, so to speak, incurred with the delivery of the heat; in fact it is like a mortgage on  $Q$ , so that we can only realize on  $Q$  in terms of energy, after deducting the liability incurred at the start. This mortgage is given by the product of the entropy of the heat delivered times the lowest available temperature; and, for a given minimum temperature, the entropy is thus the measure of the liability or, as Swinburne\* calls it: "the measure of the incurred waste"; that is, the measure of the unavoidable waste incurred in advance when the heat  $Q$  was delivered to the working substance. The word *unavoidable* is most important in this connection, for it is only in a strictly reversible change that the waste reaches this ideal minimum. In all actual engines the waste is greater, which implies a gain in the entropy during the process. But such an increase might be regarded as avoidable, for we can always reduce it by approximating more and more closely to perfect reversibility, and in that limiting case there is, therefore, no increase in the entropy during the process; for, in such a process, all the waste that is to occur is, we may say, taken on at once, when the energy that is to be utilized is supplied to the engine.

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\* "Entropy," James Swinburne; published by A. Constable & Co., London.

**Reversibility Defined in Terms of Entropy.**—We can now give a new definition of reversibility which will be most useful. A *reversible* change is one in which there is no gain in the total entropy of the system, and an *irreversible* change always involves a gain in the entropy of the system. Thus friction causes a gain in the entropy of a moving system, and heat carried by conduction also causes such a gain, both being essentially irreversible processes.

This does not mean that a *portion* of a system may not gain in entropy during a reversible change. Thus the working substance supposed in the ideal engine gains entropy when it takes heat from the generator, but if the process is reversible the generator loses an exactly equal amount. Later the substance gives up the same entropy to the refrigerator, because, as we have seen,  $\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$  or  $S_1 = S_2$ ; hence if we regard the generator, the substance, and the refrigerator as parts of one system, the entropy has simply passed unchanged from one portion of the system to another. At the lower level it will be noticed that, as a measure of incurred waste, the entropy  $\frac{Q_2}{T_2}$  indicates an incurred waste of  $Q_2$  or an efficiency equal to zero, which means that the heat delivered to the refrigerator is wholly unavailable, since  $T_2$  is supposed to be the lowest available temperature.

**Availability.**—Regarding entropy as a measure of the mortgage on the heat supplied, it is evident that the utility of a certain quantity of heat is not a constant quantity, as might at first sight appear to be the case in consequence of the law of the conservation of energy.

Its utility depends upon its entropy  $\frac{Q}{T}$  which is seen to vary inversely with the temperature at which  $Q$  is supplied. Therefore to render the "mortgage" as small as possible, it is clearly desirable to supply the heat at as high a temperature as possible; or, what is the same thing, with a minimum of entropy; and then during the process of conversion of this heat into mechanical energy, the entropy should be kept down as near the original unavoidable value as is practicable.

Care should be taken to note that this general notion of keeping the initial entropy down, supposes a certain given quantity of heat that is to be supplied. But it would be absurd to refuse an increase in this quantity on the ground that that would involve a greater initial entropy, as if one should refuse the gift of a large house with a ten per cent mortgage on it, and accept a smaller one mortgaged at the same rate, because it involved a smaller indebtedness. There are many cases indeed where it does not pay to raise the initial temperature too high, because in so doing the actual quantity of heat supplied is excessively reduced. A slight decrease in  $Q$ , however, is permissible if we have a certain amount of energy we wish to obtain, for

$$Q_1 = \left( \frac{T_1}{T_1 - T_2} \right) (Q_1 - Q_2) = \left( \frac{T_1}{T_1 - T_2} \right) K$$

where  $K$  is supposed constant. As  $T_1$  increases the quantity in the parenthesis diminishes toward unity at the limit. Thus  $Q_1$  diminishes also. This rate of decrease is considerable for small ranges of temperatures, hence in such cases raising  $T_1$  even at the expense of  $Q_1$  is permissible if the sacrifice is not too great. But such

discussions belong to the province of engineering and cannot be considered here at greater length.

**The Measurement of Entropy.**—Since we cannot regard the absolute zero as an available temperature, it is not customary to consider the *absolute entropy* of a body. But we can always determine an increase or decrease of entropy from any assigned initial condition. We are thus led to the following definition by which *entropy differences* are to be measured. When a body receives an amount of heat  $dQ$ , at a temperature  $T$ , the gain in entropy is  $dQ/T$ , and the total gain between two states,  $A$  and  $B$ , provided we can pass from one to the other by a reversible path, is  $S = \int_A^B dQ/T$ , in which  $T$  may vary, since the temperature tends to rise when heat is added to a body. This integral is merely an extension of the definition given some pages back. It assumes that each infinitesimal quantity of heat  $dQ$  is given to the body at some temperature  $T$ , and that the resulting change in the state of the body is a reversible one, so that there will be no growth of entropy except as it increases by the continual gain in  $Q$  from the external source. This rules out such irreversible increases in temperature as that due to the eddy currents which are set up in a receiver when hot water is run into it. It is clear that  $\int dQ/T$  over a reversible path is a highly ideal function that can never be realized in practice. Its value, however, as a measure of the unavailable energy of a given supply of heat, is not diminished by that fact. For instance if we accurately plotted a curve between  $Q$  and  $\frac{1}{T}$  as we heated a certain

mass of water from  $T_1$  to  $T_2$ , and then measured its area, that area would be proportional to the actual entropy supplied to the water when heated. But owing to radiation losses, etc., this area would be greater than under ideal reversible conditions, and therefore greater than the integral  $\int_{T_2}^{T_1} dQ/T$  over the reversible path when no radiation would be allowed for. This integral, however, measures the actual difference of entropy between water at  $T_1$  and at  $T_2$ . This can be made clear by an analogy from mechanics; in measuring the gravitational potential of a point above a certain level taken as zero, we take the product of the vertical height by the force due to gravity acting on the unit mass, although the actual work done in raising the unit mass to that level may be greater owing to air friction. This error might be made as small as we choose, and thus the true potential, or  $gh$ , is the limiting case when we measure the actual work in conveying the unit mass to the point in question.

Thus the difference of entropy between the states  $A$  and  $B$  is measured by  $\int_A^B dQ/T$ , provided the integral is taken over a reversible path, and this will be always assumed to be the case. This integral gives a value less than the entropy supplied to the body in passing between the initial and final states when the path followed is an irreversible one. In other words, more entropy may be taken on by a body in passing from  $A$  to  $B$  than the difference of entropy between those states as measured by a reversible process; therefore the entropy supplied to the body depends on the path, while the difference of

entropy between the initial and final states is a constant independent of the path. These two aspects of entropy, one, the amount absorbed by the body, and the other, the measure of the difference between the two states, have their equivalents in *actual work done* and the *difference of potential* between two points, and they are only equal when the path followed is a reversible one. It will, in future, be understood, that  $\Delta S$  refers to the former, and  $\int \frac{dQ}{T}$  to the latter.

**Isentropic Lines.**—During any adiabatic transformation, no heat enters or leaves the body, and, unless heat be supplied from within,  $dQ = 0$ , or  $dQ/T = 0$ , hence  $Q/T$  is constant. An adiabatic is therefore usually regarded as a line of constant entropy, and is often called an isentropic. If the adiabatic change is irreversible, there will be an internal gain in entropy due to friction or other causes, therefore the entropy of a body changing adiabatically is only constant in the limiting case of perfect reversibility. But in all cases we are justified in the statement that no entropy is added to, or taken from the body through its bounding surface during an adiabatic change.

**Clausius' Extension of Carnot's Principle.**—As we have seen (p. 44), the working substance in a Carnot cycle during an isothermal compression parts with the same amount of entropy that it gained during the isothermal expansion; hence at the end of the cycle its entropy is exactly where it was before. This we have expressed by writing  $\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$ . Therefore around a Carnot cycle we may write for the working sub-



stance  $\Sigma \frac{Q}{T} = 0$ . This proposition is readily extended to the case of a body being carried through any reversible cycle. For we may map out the area enclosed by any contour  $A B$  in elementary Carnot cycles as indicated, and the area enclosed by the zigzag contour  $a b c \dots c' b' a'$  . . . is made up of elementary cycles that may be made as narrow as we wish. Now the sum of the changes of entropy around the cycle  $a \alpha$

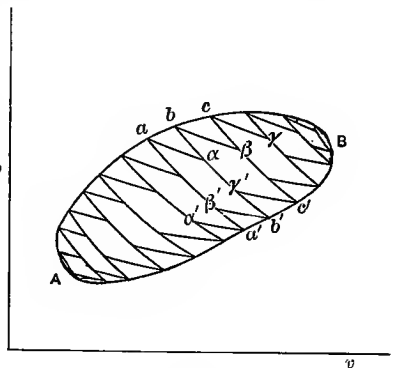


FIG. 14.

$b' \beta'$  is zero, or  $\Sigma \frac{Q}{T} = 0$ . Similarly around the cycle  $b \beta c' \gamma' = 0$ , also in the cycle around both, *i.e.*,  $a \alpha b \beta c' \gamma' b' \beta'$  we have  $\Sigma \frac{dQ}{T} = 0$  for the only portion that is left out in following this longer route is  $\alpha \gamma'$  which is a portion of a reversible adiabatic and so introduces no change in entropy. The triangle-like areas,  $a \alpha b$ ,  $b \beta c$ , etc., that have been neglected, represent a vanishing quantity when the number of Carnot cycles is made indefinitely great. This is readily seen by considering the fact that the value of  $\Sigma \frac{Q}{T}$  around a "triangle" is represented by the gain in entropy in passing along  $a b$ , less the loss in passing along  $a \alpha$ , there being no change in going from  $b$  to  $\alpha$ , which was taken as a reversible adiabatic.

This difference is not zero for a path of finite dimensions, although it would be small, but it may be made to vanish by taking the series of adiabatics infinitely close together, their area thus becoming a differential of the first order, while the "triangles" become differentials of the second order and may be neglected.

**Various Forms of the First and Second Laws.**—We are thus justified in writing  $\int \frac{dQ}{T} = 0$  taken over any closed path representing a reversible cycle. This equation depends upon the relation  $\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$ , which was derived from Carnot's principle, and that in turn from the second law of thermodynamics, therefore the statement  $\int \frac{dQ}{T} = 0$  around a closed reversible path expresses the second law in a concise mathematical form, and will be much used in what follows.

The first law of thermodynamics may be similarly expressed by the equation  $\int dQ = W$ , where the integration is carried around the cycle and  $W$  is the work done. This is evident because, as has already been shown, the algebraic sum of the heat taken in and the heat rejected gives us the heat that disappears during a cycle, and this lost heat, by the first law of thermodynamics, is proportional to the mechanical work done.

**Exact Differential.**—A final statement of the second law consists in the remark that during a reversible process  $dS$ , or  $dQ/T$ , is an exact differential. This is true of all differentials whose integration over a closed path is equal to zero. This principle has already been

explained in the case of internal energy, and we may repeat the same conclusion concerning entropy, that the gain or loss of entropy of a body in passing from the state  $A$  to the state  $B$  by a reversible path is independent of the particular path followed, and depends only on the initial and final states. It is interesting to note that the same is true of gravitational and electrostatic potentials. In fact the very notion of a potential function involves this property. To sum up the various statements of the first and second laws, they may be tabulated as follows:

FIRST LAW.	SECOND LAW.
1. Exact proportionality of all transformations of energy.	1. Heat cannot flow unaided from lower to higher temperatures.
2. $dQ = dW + dU$ .	2. Carnot's principle of the efficiency of a reversible engine, <i>i.e.</i> , $E = \frac{T_1 - T_2}{T_1}$
3. $\int dQ = W$ around any closed reversible path.	3. $\int \frac{dQ}{T} = 0$ around any closed reversible path.
4. $dU$ = an exact differential for all reversible changes.	4. $dS$ = an exact differential for all reversible changes.

**Combination of First and Second Laws.**—Both laws may be expressed in a single equation; thus, since  $dS = dQ/T$  (second law), we have

$$dQ = T dS$$

but  $dQ = dW + dU$  (first law), hence  $T dS = dW + dU$ , which may be regarded as the fundamental equation

of thermodynamics, since it involves both its fundamental postulates.

This equation may be written slightly differently in all cases where the work  $dW$  is done against the kind of pressure we have called "hydrostatic." In this special, but very common case,  $dW = p dV$ , where  $dV$  is the change in volume of the expanding medium or body, thus we have,

$$T dS = p dV + dU \quad . \quad . \quad . \quad (27)$$

**Special Case Where  $T$  is Constant.**—There is one important particular case of the integration  $\int \frac{dQ}{T}$  taken around a closed path, which occurs when  $T$  is constant. It follows that  $\frac{1}{T} \int dQ = 0$ , or, since  $T$  cannot be infinite,  $\int dQ = 0$ , hence

$$\int dQ = \int dU + \int dW = 0, \text{ or } U_2 - U_1 + \int dW = 0$$

but  $U_2 = U_1$  when the cycle is complete, so we arrive at the conclusion that  $\int dW = 0$ ; that is, the external work done in carrying a body through an isothermal, reversible cycle is zero.

**Irreversible Cycles.**—The cycles thus far considered in detail have been reversible. In case, however, the cycle is irreversible (and this must always be more or less so in practice), Clausius showed that  $\int \frac{dQ}{T} < 0$ . This is known as the *Inequality of Clausius*, and is easily proved. It has already been pointed out that the entropy gained in passing from one state to another by

an irreversible path is greater than by a reversible one. This may be expressed symbolically as follows: let  $R$  be the unavailable energy of any transformation, then  $R = T_o \Delta S$  where  $T_o$  is the lowest available temperature. Also let  $R_r$  = the unavailable energy of a reversible transformation, then  $R_r = T_o \int dQ/T$ . But in general  $R \geq R_r$  because it follows from Carnot's principle that the reversible process is the most efficient.  $\therefore \Delta S \geq \int \frac{dQ}{T}$

Let  $A$  and  $B$  designate the states at the beginning and end of an irreversible transformation, then we may write  $\Delta S_A^B > \int_A^B \frac{dQ}{T}$  and similarly on returning to the original state,  $\Delta S_B^A > \int_B^A \frac{dQ}{T}$ , but  $\Delta S_A^B = -\Delta S_B^A$  because obviously the body must get rid of the entropy gained in going from  $A$  to  $B$ , on its return to  $A$  again, hence adding these inequalities  $\int \frac{dQ}{T} < 0$  taken around the cycle.

The exact meaning of this inequality is that in going through the irreversible cycle, an amount of entropy equal to  $\int dQ/T$  must be withdrawn from the body in order to compensate for an irreversible gain of the same amount, so that the body may be brought back to the original state.

Another way of stating the inequality of Clausius is the following. Since, as has been shown, we may pass from  $A$  to  $B$  by means of a series of infinitesimal adiabatic and isothermal changes, and since each step is reversible, it follows that *any reversible path may be so decomposed.*

Hence the gain in entropy in passing from  $A$  to  $B$  reversibly may be compensated by returning over any reversible route, such as one adiabatic and one isothermal step. If, however, the path from  $A$  to  $B$  is irreversible, it cannot be decomposed into a series of reversible steps, nor can it be correctly represented on the  $p-v$  diagram; and therefore the greater gain in entropy involved cannot be compensated by a reversible return path, while an irreversible return would remove even less of the gained entropy and, therefore, *a fortiori*, *it is impossible completely to compensate the entropy gained by an irreversible change.*

**Tendency of the Entropy of a System Toward a Maximum.**—Another interesting aspect of non-reversible processes is when we are concerned with a system of bodies at different temperatures, and so disposed that heat can flow from the hotter to the colder either by radiation or conduction. If we consider a body whose temperature is  $T_1$ , and allow a quantity of heat,  $dQ$ , to flow from it to another body whose temperature is  $T_2$ , then the initial entropy of the system is diminished by  $dQ/T_1$ , and increased by  $dQ/T_2$ , hence the net gain is  $dQ\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$  which is a positive quantity since  $T_2 < T_1$  by hypothesis. This is readily extended to the case of any number of bodies, for, whatever the final temperature of the system, it is certain that each transfer of heat is from a hotter to a colder body, and therefore represents a gain in entropy. This means that such a system, if left to itself, tends toward a maximum of entropy, and consequently of unavailable energy; and when this maximum is reached, the available

energy vanishes, or, what is the same thing, the component parts of the system are all at the same temperature. This, it may be remarked, is the natural tendency of our universe under the process of radiation among its component parts. If it is regarded as a self-contained system, it is tending inevitably toward the condition of thermal equilibrium indicated above.

**Thermodynamic Variables.**—The quantities we have so far discussed, are the external work  $W$ , the quantity of heat  $Q$ , the internal energy  $U$ , and the four variables,  $V$ ,  $p$ ,  $T$ , and  $S$ , any two of which may be taken as independent in thermodynamic equations. As Maxwell pointed out,  $W$ ,  $V$ , and  $p$  are quantities related to external work, while  $Q$ ,  $S$ , and  $T$  refer to thermal energy, and there is a striking correspondence in the pairs  $W$  and  $Q$ ,  $V$  and  $S$ ,  $p$  and  $T$ , as is evident from the analogous equations,

$$\begin{aligned}dW &= p dV \\dQ &= T dS.\end{aligned}$$

We might put this somewhat crudely in words by calling temperature “thermal pressure,” and entropy “thermal volume.”

**Heat and Work Diagrams.**—Evidently if we use  $T$  and  $S$  as the co-ordinates of a diagram representing any transformation, the area will be proportional to  $Q$ , for  $\int dQ = \int T dS$ , which is thus an area integral of the form  $\int y dx$ . But it should be carefully noted that this is only true when this diagram refers to a reversible process, for in irreversible processes  $\int dQ < \int T dS$ ,

and the area of the diagram is larger than what would correspond to the heat absorbed or rejected by the working substance during the transformation. The same is true of the  $p v$  diagram, which represents the external work done when that work is performed reversibly against a uniform normal pressure, but if the process is irreversible, the area of the diagram is too large. An illustration of this would be the case of a viscous working fluid which would expand slowly as the pressure fell, so that the actual pressure on the piston would always be less than the pressure within the fluid, and consequently the work done would be less than that recorded by an indicator.

**Thermodynamic Potential.**—The quantity  $U$  has so far been regarded as the intrinsic energy of the system, due partly to the kinetic energy represented by the temperature, and partly to the state of disgregation of the molecules. But, as in the case of mechanics, this energy has two aspects. We may regard it from the standpoint of the work put into the body to bring it to the state considered, or we may regard it as the ability to perform work by virtue of its thermal condition. Viewed from this latter standpoint, it is called *Thermodynamic Potential*, and we shall use the letter  $F$  to represent it in this aspect. But  $U$  is not the only function that may be regarded as a potential. In fact there are four such quantities, and following Bryan,\* we shall call them  $F_{SV}$ ,  $F_{TV}$ ,  $F_{TP}$ ,  $F_{SP}$ , the subscripts indicating the independent variables in which they are expressed.  $F_{SV}$  is the potential of  $U$ , for  $dU = T dS - p dV$ , as has been shown.

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\* Bryan, "Thermodynamics." Teubner Texts.



The other functions were first determined by Massieu as follows: Starting with (27)  $dU = T dS - p dV$ , but  $d(TS) = T dS + S dT$ , substituting for  $T dS$  gives  $dU - d(TS) = -S dT - p dV$ , or,  $d(U - TS) = -S dT - p dV$ , writing  $(U - TS) = F_{TV}$ , which is Gibbs'  $\psi$  function, we obtain

$$dF_{TV} = -S dT - p dV \quad . \quad . \quad . \quad (28)$$

Since by definition,

$$dF_{TV} = d(U - TS)$$

$$dF_{TV} = dU - d(TS).$$

It is thus evident that  $dF_{TV}$  is an exact differential just as  $dF_{SV}$  (or  $dU$ ) has been shown to be exact. This is made particularly clear in the last expression which shows it to be equal to the difference of two exact differentials.

Similarly if we start with  $d(pV) = p dV + V dp$ , we have, by substitution in equation (27),

$$dU + d(pV) = T dS + V dp$$

next set  $F_{Sp} = (U + pV)$ , which is Gibbs'  $\chi$  function, or

$$dF_{Sp} = T dS + V dp \quad . \quad . \quad . \quad (29)$$

This is also an exact differential like the two preceding, for  $dF_{Sp} = dU + d(pV)$ , and is the sum of two exact differentials.

Finally, using both substitutions, simultaneously gives us  $dU + d(pV) - d(TS) = V dp - S dT$ , setting  $F_{Tp} = (U + pV - TS)$ , we obtain Gibbs'  $\zeta$  function, or

$$dF_{Tp} = V dp - S dT \quad . \quad . \quad . \quad (30)$$

which is easily seen to be an exact differential by definition, like the three preceding.

When discussing thermodynamic potential, ordinarily, either  $F_{TV}$  or  $F_{Tp}$  are used, and they may be called the thermodynamic potentials at given volume, and at given pressure respectively.

**Equilibrium and Stability.**—The various potential functions we have been discussing are related to the stability of a body, or a system of bodies, just as mechanical potential energy is related to gravitational equilibrium. It is a consequence of the general principle called “degradation of energy” that all unaided changes within a system must be irreversible changes. An unaided flow of heat involves a transfer from a hotter body to a colder which is an irreversible process; and all such mechanical changes involve more or less friction and are therefore irreversible. Now, if an irreversible change involves the decrease of a certain function, it means that all unaided changes within the system must tend to diminish that function; and the system will only have reached stable equilibrium when that function is at a minimum, or, in other words, if any small change within the system can only result in an increase of the value of that function, the system is in stable equilibrium within the limits of said small change. Suppose we consider first how stability may be determined by the potential  $U$ .  $U$  is defined by the equation  $dU = dQ - p dV$ , but in all irreversible changes,  $dQ < T dS$   $dU < T dS - p dV$  for all changes that can occur automatically. If we suppose our system surrounded by a perfectly rigid envelope impervious to heat, then the total volume is constant or  $\Sigma dV = 0$ , taken over the system, and since, as a whole, the system is adiabatic  $\Sigma T dS = 0$ , hence it follows that  $\Sigma dU < 0$  for all

possible automatic changes within the system; or we may state that when equilibrium has been reached, and  $U$  is a minimum, then any possible change must tend to increase  $U$ , or  $dU > 0$ , which is one of Gibbs' criteria of stability.

In a similar manner we may examine the other thermodynamic potentials. Thus  $dF_{TV} = d(U - TS) = dU - TdS - SdT$  by definition, but  $dQ < TdS$  for irreversible or unaided changes

$$dF_{TV} < dU - dQ - SdT$$

but  $dU - dQ = -pdV$

$$dF_{TV} < -pdV - SdT.$$

But if our system is now considered as surrounded by a rigid envelope and the whole maintained at a constant temperature, then  $\Sigma dV = 0$  and  $\Sigma dT = 0$  taking the sum over the whole system, hence  $dF_{TV} < 0$  for all unaided changes and for equilibrium all possible changes must increase  $F_{TV}$ ; or  $dF_{TV} > 0$  is the criterion of stability of such a system.

In like manner  $dF_{Tp} > 0$  is the criterion of stability of a system whose temperature and pressure are constant. This criterion is applicable to the particular case of evaporation of a liquid under constant pressure which process results in a decrease of its potential energy and  $F_{Tp}$  will only reach a minimum indicating stability when all the liquid is vaporized.

By a similar process of reasoning  $dF_{Sp} > 0$  may be shown to be a fourth criterion of stability.

**Available Energy.**—Still another test of stability results from the principle already pointed out, that unaided changes within a system must be irreversible

changes, and therefore involve an increase of entropy of the system; or, what is the same thing, a decrease in its available energy.

Let us consider the available energy of a system surrounded by a medium whose temperature and pressure are constant and equal to  $T_o$  and  $p_o$ . Such a system can lose available energy either by a loss of heat, or fall of internal pressure, or both. Suppose a change occurs within the system involving a disappearance of an amount of heat  $dQ_1$  with a corresponding production of work. The energy available for work cannot be greater than  $dQ_1 \frac{T_1 - T_o}{T_1}$  where  $T_1$  is the temperature of the portion whose heat is reduced. On the other hand if the system lose available energy by expansion, the loss is  $(p_1 - p_o) dV_1$ , where  $p_1$  is the pressure of the portion that expands by an amount  $dV_1$  against the surrounding pressure  $p_o$ . Since the available energy may vary in both these ways, its total differential is

$$[dA]_{Tp} = dQ_1 \left( \frac{T_1 - T_o}{T_1} \right) + (p_1 - p_o) dV_1$$

for any portion of the system. But  $\frac{dQ_1}{T_1} = dS_1$  which reduces the above equation to  $[dA]_{Tp} = (T_1 - T_o) dS_1 + (p_1 - p_o) dV_1$  and further, by equation (27),  $dU_1 = T_1 dS_1 - p_1 dV_1$  hence, introducing  $J$ ,

$$[dA]_{Tp} = dU_1 - T_o dS_1 + p_o dV_1/J. \quad (31)$$

But by definition  $[dF_{Tp}]_{Tp} = dU_1 - T dS_1 + p dV_1$ ; therefore, if the temperature and pressure of the medium that surrounds the system, whose potential is  $F_{Tp}$ , are  $T_o$  and  $p_o$ , it follows that  $F_{Tp}$  is a measure of the available

energy of such a system surrounded by such a medium. It has, therefore, been called by Duhem the "*total thermodynamic potential*." If, however, we suppose the volume and temperature to be constant, the general expression for available energy becomes:

$$[dA]_{TV} = dU_1 - T_o dS_1 \quad . \quad . \quad . \quad (32)$$

but  $[dF_{TV}]_{TV} = dU - T dS$ , hence if the system be enclosed in a rigid envelope whose temperature is constant, the potential at constant volume is a measure of its available energy. This potential was called the "*free energy*" of the system by Helmholtz, and the "*inner thermodynamic potential*" by Duhem.

In case the entropy and pressure are constant,

$$[dA]_{Sp} = dU_1 + p_o dV_1/J \quad . \quad . \quad (33)$$

which is equal to the partial differential of the potential  $F_{Sp}$  at constant pressure and entropy for the same value of the constants assumed.

Finally, if the system is enclosed in a rigid envelope, impermeable to heat,  $T dS = 0$ , and

$$[dA]_{SV} = dU_1 \quad . \quad . \quad . \quad (34)$$

hence, in such an isolated system, the available energy is equal to the intrinsic energy. Of course, in this case, as in those that precede it, we cannot evaluate  $\int dU$  except between two arbitrarily chosen values as  $U_1$  and  $U_2$  giving  $A_{SV} = U_1 - U_2$ .

Similarly  $A_{Tp} = U_1 - U_2 + (V_1 - V_2) p_o - (S_1 - S_2) T_o$

Similarly  $A_{TV} = U_1 - U_2 - (S_1 - S_2) T_o$

Similarly  $A_{Sp} = U_1 - U_2 + (V_1 - V_2) p_o$

Since in these cases just specified, in general  $A = F$ , we may add the further criterion of stability that any possible change in the system, when it is in equilibrium, must result in an increase of available energy. Or: *for stability  $A$  is a minimum.*

## CHAPTER IV

### THERMODYNAMIC EQUATIONS

FROM the two laws of thermodynamics, and the fundamental relations between the heat capacities already established in Chapter I, a great variety of general formulæ may be derived. We shall, however, content ourselves at present with the derivation of the most important only, and others will be developed as they are needed, in the discussion of the particular cases of gases, vapors, etc.

**Maxwell's Relations.**—There are four important relations between the various differential coefficients of the variables  $p$ ,  $v$ ,  $T$ , and  $S$ , called the four relations of Maxwell. These are readily derived from the thermodynamic potentials as follows.

**Maxwell's First Relation.**—By equation (27), for reversible processes

$$dU \text{ or } dF_{SV} = T dS - p dV$$

but  $dU$  is an exact differential, and, applying the usual criterion of such functions to the right-hand member, we have

$$\left(\frac{dT}{dV}\right)_S = -\left(\frac{dp}{dS}\right)_V \quad . \quad . \quad . \quad (35)$$

which is known as *Maxwell's first relation*. This equation can be transformed by writing  $\frac{dQ}{T} = dS$  and, taking the unit mass, we have

$$\left(\frac{dT}{dv}\right)_q = -T\left(\frac{dp}{dq}\right)_v = -\frac{T}{\eta}, \text{ or} \\ \eta = -T\left(\frac{dv}{dT}\right)_q \quad . \quad . \quad . \quad . \quad (36)$$

A special case of interest arises during an adiabatic change, or when  $dQ = 0$ . By equation (4)  $c dT + l dv = 0$ , or  $\left(\frac{dv}{dT}\right)_q = -\frac{c}{l}$ . Combining with (36) it becomes

$$\left[\eta = \frac{Tc}{l}\right]_q \quad . \quad . \quad . \quad . \quad (37)$$

**Maxwell's Second Relation** is obtained from equation (29)  $dF_{Sp} = T dS + V dp$  which, by the principle of exact differentials, gives

$$\left(\frac{dT}{dp}\right)_s = \left(\frac{dV}{dS}\right)_p \quad . \quad . \quad . \quad . \quad (38)$$

This is *Maxwell's second relation* and may be transformed as in the previous case to

$$\left(\frac{dT}{dp}\right)_q = T\left(\frac{dv}{dq}\right)_p = \frac{T}{\lambda}; \text{ or } \lambda = T\left(\frac{dp}{dT}\right)_q \quad (39)$$

During an adiabatic change, by equation (3),  $C dT + h dp = 0$ , or  $\left(\frac{dp}{dT}\right)_q = -\frac{C}{h}$ , combining this with (39) gives:

$$\left[\lambda = -\frac{TC}{h}\right]_q \quad . \quad . \quad . \quad . \quad (40)$$

**Maxwell's Third Relation** follows in the same manner from (28),  $dF_{TV} = -S dT - p dV$ , giving

$$\left(\frac{dS}{dV}\right)_T = \left(\frac{dp}{dT}\right)_V \quad . \quad . \quad . \quad . \quad (41)$$



which may be transformed, taking unit mass, to

$$\left(\frac{d q}{d v}\right)_T = T \left(\frac{d p}{d T}\right)_v, \text{ or } l = T \left(\frac{d p}{d T}\right)_v \quad (42)$$

In this latter form, *Maxwell's third relation* is usually called the equation of Clapeyron, and is of great value in many applications of thermodynamics where a body is undergoing a change of state, like melting ice, or boiling water, when the so-called "latent heat" is added at constant temperature, the body in general undergoing a change in volume expressed by  $\left(\frac{d Q}{d V}\right)_T$ . It should be carefully noted that  $l$  is not the latent heat as usually defined; " $L$ ," the ordinary latent heat, is the quantity necessary to completely transform from one state to another the unit mass at constant temperature, while  $l$  is the heat per unit change in specific volume; therefore  $l d v = d L$  and the equation of Clapeyron may take the form

$$L = T \left(\frac{d p}{d T}\right) (v_2 - v_1) \quad (43)$$

where  $v_1$  and  $v_2$  are the specific volumes before and after the change of state.

**Maxwell's Fourth Relation** follows from equation (30), or  $d F_{Tp} = V d p - S d T$ , giving

$$\left(\frac{d S}{d p}\right)_T = - \left(\frac{d V}{d T}\right)_p \quad (44)$$

which is the *fourth relation*, and is readily transformed as in the preceding cases to

$$\left(\frac{d q}{d p}\right)_T = - T \left(\frac{d v}{d T}\right)_p, \text{ or } h = - T \left(\frac{d v}{d T}\right)_p \quad (45)$$

Another form of this fourth relation may be obtained by substituting  $\alpha_p = \frac{1}{v} \left( \frac{dv}{dT} \right)_p$  giving

$$\left( \frac{dq}{dp} \right)_T = -T v \alpha_p \quad . \quad . \quad . \quad (46)$$

This means that if a body expands when heated under constant pressure, that is, if  $\alpha_p$  is positive, then  $\frac{dq}{dp}$  is negative, or heat must be withdrawn with increasing pressure, in order to maintain the temperature constant.

On the other hand, if  $\alpha_p$  is negative, heat must be added to keep  $T$  constant. Joule showed that this prediction was verified in the case of water at temperatures above and below  $4^\circ \text{C}$ . Compression above  $4^\circ \text{C}$ . causes a rise of temperature, while below  $4^\circ$ , it causes a fall.

**Relations Between the Specific Heats.**—By applying the two laws of thermodynamics to the general expressions that define the heat capacities, we may obtain various useful relations between these quantities.

In Chapter I, we proved in equation (7) that  $C - c = -h \frac{\delta p}{\delta T}$ , or  $h = -(C - c) \frac{\delta T}{\delta p}$ . Substituting this value of  $h$  in equation (3) we obtain

$$dq = C dT - (C - c) \frac{\delta T}{\delta p} dp, \quad . \quad . \quad (i)$$

but by our fundamental hypothesis (1), we know that  $T = f(p, v)$ .

$$\therefore dT = \frac{\delta T}{\delta v} dv + \frac{\delta T}{\delta p} dp$$

substituting this in (i) above, we have

$$d q = C \left( \frac{\partial T}{\partial v} d v + \frac{\partial T}{\partial p} d p \right) - (C - c) \frac{\partial T}{\partial p} d p$$

which reduces to

$$d q = C \frac{\partial T}{\partial v} d v + c \frac{\partial T}{\partial p} d p \quad . \quad . \quad (47)$$

If we subtract  $p d v$  from both sides of the equation, remembering that  $d q - p d v = d u$ , we obtain

$$d u = \left( C \frac{\partial T}{\partial v} - p \right) d v + c \frac{\partial T}{\partial p} d p \quad . \quad (ii)$$

which, in consequence of the first law of thermodynamics, is an exact differential. Another exact differential can be obtained from (47) by dividing through by  $T$ , giving

$$d s = \frac{C}{T} \left( \frac{\partial T}{\partial v} \right) d v + \frac{c}{T} \frac{\partial T}{\partial p} d p \quad . \quad . \quad (iii)$$

which, in consequence of the second law, is an exact differential also. Operating on (ii) and (iii), according to the usual method with exact differentials, we obtain

$$\frac{\partial C}{\partial p} \frac{\partial T}{\partial v} + C \frac{\partial^2 T}{\partial v \partial T} - 1 = \frac{\partial c}{\partial v} \frac{\partial T}{\partial p} + c \frac{\partial^2 T}{\partial v \partial T} \quad (iv)$$

and

$$\begin{aligned} \frac{\partial C}{T \partial p} \frac{\partial T}{\partial v} - \frac{C}{T^2} \frac{\partial T}{\partial p} \frac{\partial T}{\partial v} + \frac{C}{T} \frac{\partial^2 T}{\partial p \partial v} = \\ \frac{\partial c}{T \partial v} \frac{\partial T}{\partial p} - \frac{c}{T^2} \frac{\partial T}{\partial p} \frac{\partial T}{\partial v} + \frac{c}{T} \frac{\partial^2 T}{\partial p \partial v} \end{aligned} \quad (v)$$

which reduces to

$$\frac{\partial C}{\partial p} \frac{\partial T}{\partial v} - \frac{(C - c)}{T} \frac{\partial T}{\partial p} \frac{\partial T}{\partial v} + \frac{C}{T} \frac{\partial^2 T}{\partial p \partial v} = \frac{\partial c}{\partial v} \frac{\partial T}{\partial p} + c \frac{\partial^2 T}{\partial p \partial v} \quad (vi)$$

Combining equations (iv) and (vi), gives us

$$\begin{aligned} \frac{C - c}{T} \frac{\partial T}{\partial p} \frac{\partial T}{\partial v} = 1 \text{ or} \\ C - c = T \frac{\partial v}{\partial T} \frac{\partial p}{\partial T} \quad . \quad . \quad . \quad (48) \end{aligned}$$

An interesting consequence of this equation occurs when a body passes through a point of maximum density while the temperature is varied. In this case  $\frac{\partial v}{\partial T} = 0$  and  $C - c = 0$ , or the specific heats become equal at this point.

If this expression for  $C - c$  is divided by equation (7), we find  $h = -T \frac{\partial v}{\partial T}$ , which is Maxwell's fourth relation, and, dividing it by equation (10), we recover Maxwell's third relation, or  $l = T \frac{\partial p}{\partial T}$ . Hence it would have been possible to derive (48) directly from Maxwell's relations and the heat capacity equations. The longer method has been used as it illustrates a very useful mode of procedure in obtaining thermodynamic equations.

Two more equations similar to (48) may be obtained in like manner. By equation (3) we have  $dq = C dT + h dp$ , which is converted into an exact differential by subtracting  $p dv$ , or  $du = C dT + h dp - p dv$ , but  $p dv = d(pv) - v dp$ , hence  $du + d(pv) = C dT + (h + v) dp$ , which, being the sum of two exact differentials, is exact also; therefore, operating as usual,

$$\frac{\partial C}{\partial p} = \frac{\partial h}{\partial T} + \frac{\partial v}{\partial T} \quad . \quad . \quad . \quad (i)$$

but by (45),  $h = -T \left( \frac{\partial v}{\partial T} \right)_p$  or

$$\frac{\partial h}{\partial T} = - \frac{\partial v}{\partial T} - T \frac{\partial^2 v}{\partial T^2} \quad . \quad . \quad . \quad (ii)$$

substituting this value of  $\frac{\partial h}{\partial T}$  in (i), we obtain

$$\frac{\partial C}{\partial p} = -T \frac{\partial^2 v}{\partial T^2} \quad . \quad . \quad . \quad (49)$$

Proceeding in exactly the same manner with equation (4), we find

$$\frac{\delta c}{\delta v} = T \frac{\delta^2 p}{\delta T^2} \quad . \quad . \quad . \quad (50)$$

As in the case of (48), equations (49) and (50) might have been obtained directly from Maxwell's relations. Thus (50) may be derived by differentiating (42), or  $l = T \frac{\delta p}{\delta T}$ , with respect to the temperature, and substituting in (24), ignoring  $J$ ; while (49) is similarly derived from equations (45) and (25).

**General Expressions for the Specific Heats.**—In the first chapter we obtained several expressions for the specific heat of a body that were independent of any hypothesis as to the nature and behavior of heat. We may now, however, by introducing Maxwell's relations, which depend upon the first and second laws, derive other expressions of more practical value.

By combining equation (4), and the equation of Clapeyron (42), and dividing through by  $d T$ , we obtain, for unit mass,

$$\frac{d q}{d T} = c + T \left( \frac{d p}{d T} \right)_v \frac{d v}{d T} \quad . \quad . \quad . \quad (51)$$

and a combination of equations (3) and (45) gives

$$\frac{d q}{d T} = C - T \left( \frac{d v}{d T} \right)_p \frac{d p}{d T} \quad . \quad . \quad . \quad (52)$$

While an expression involving both  $C$  and  $c$  is obtained from (47) by dividing by  $d T$  giving

$$\frac{d q}{d T} = C \left( \frac{d T}{d v} \right)_p \frac{d v}{d T} + c \left( \frac{d T}{d p} \right)_v \frac{d p}{d T} \quad . \quad (53)$$

**Equations Involving Thermodynamic Potential.**—It was first pointed out by M. F. Massieu (1869-1876) that any coefficient determining the nature of a body such as  $h$ ,  $l$ ,  $C$ ,  $c$ , etc., can be expressed as a function of any one of the potentials we have defined. Therefore, if we know any potential function of a body, we are able to determine all its characteristics. It is, then, most important, not only to be able to determine these potentials, but also to deduce the relations that exist between them, and the various coefficients.

Moreover, the independent variables may be expressed as functions of the partial derivatives of the potential functions. These latter relations are almost self-evident; thus we obtain directly from the defining equation of  $U$  in reversible processes, or  $dU = T dS - p dV$ ,

$$\left(\frac{dU}{dS}\right)_v = T \quad . \quad . \quad . \quad . \quad (54)$$

and

$$\left(\frac{dU}{dV}\right)_s = -p \quad . \quad . \quad . \quad . \quad (55)$$

Equation (54) may be written  $\left(\frac{dU}{dQ}\right)_v = 1$ , by setting

$dS = \frac{dQ}{T}$  In this form it shows that when the volume is constant, the intrinsic energy varies directly with the heat received, or

$$[dU = dQ]_v \quad . \quad . \quad . \quad . \quad (56)$$

Equation (55) shows that during an adiabatic expansion, the intrinsic energy decreases at the expense of the pressure. In deducing similar relations with the other potentials, we shall write for simplicity  $F = F_{TV}$  and  $F' = F_{Tp}$ .

Taking the defining equation of  $F$ , (28), or  $dF = -S dT - p dV$ , it follows that

$$\left(\frac{dF}{dT}\right)_V = -S, \text{ and } \left(\frac{dF}{dV}\right)_T = -p \quad (57)$$

From (29),  $dF_{Sp} = T dS + V dp$ , two similar relations are obtained, or:

$$\left(\frac{dF_{Sp}}{dp}\right)_S = V, \text{ and } \left(\frac{dF_{Sp}}{dS}\right)_p = T \quad (58)$$

and from (30), or  $dF' = V dp - S dT$ , we have

$$\left(\frac{dF'}{dT}\right)_p = -S, \text{ and } \left(\frac{dF'}{dp}\right)_T = V \quad (59)$$

Also since  $F = U - TS$ , by substituting for  $S$  from equation (57)

$$U = F - T \left(\frac{dF}{dT}\right)_V \quad (60)$$

which shows the possibility of finding inter-relations between the various potentials and their derivatives.

A relation similar to (60), but between  $U$  and  $F'$ , can be obtained from the defining equation of  $F'$ , (30); substituting for  $S$  and  $V$  their values as found in equation (59), we obtain

$$U = F' - T \left(\frac{dF'}{dT}\right)_p - p \left(\frac{dF'}{dp}\right)_T \quad (61)$$

We are now able to determine the specific heats and other characteristic coefficients. Since by definition  $c = \left(\frac{dq}{dT}\right)_v$  and  $dq = T ds$ , we have  $\left(\frac{dq}{dT}\right)_v = T \left(\frac{ds}{dT}\right)_v$ . Now differentiate  $S$  in equation (57) with respect to  $T$ , keeping

$v$  constant, and substitute for  $\left(\frac{ds}{dT}\right)_v$  its value just obtained, and we have for unit mass

$$c = \left(\frac{dq}{dT}\right)_v = -T \left(\frac{d^2 f}{dT^2}\right)_v \quad . \quad . \quad . \quad (62)$$

where  $f$  indicates the value of  $F$  for unit mass. To find  $C$  in terms of  $f$ , take equation (48); but it was shown on page 13 that

$$\left(\frac{dT}{dv}\right)_p \left(\frac{dp}{dT}\right)_v = -\left(\frac{dp}{dv}\right)_T,$$

therefore (48) may be transformed to

$$C - c = -T \left(\frac{dp}{dT}\right)_v^2 \bigg/ \left(\frac{dp}{dv}\right)_T$$

but by (57),  $p = -\left(\frac{df}{dv}\right)_T$ , hence,

$$C - c = T \left(\frac{\delta^2 f}{\delta T \delta v}\right)^2 \bigg/ \left(\frac{d^2 f}{dv^2}\right)_T \quad . \quad . \quad (62')$$

or substituting the value of  $c$  already found, we have

$$C = -T \left(\frac{d^2 f}{dT^2}\right)_v + T \left(\frac{\delta^2 f}{\delta T \delta v}\right)^2 \bigg/ \left(\frac{d^2 f}{dv^2}\right)_T \quad (63)$$

$l$  may also be expressed in terms of  $f$ , for, by definition,  $l = \left(\frac{dq}{dv}\right)_T$ , hence by aid of (57), we obtain

$$l = \left(\frac{dq}{dv}\right)_T = T \frac{\delta s}{\delta v} = -T \frac{\delta^2 f}{\delta T \delta v} \quad . \quad (64)$$

Similarly  $h = \left(\frac{dq}{dp}\right)_T$ , but by equation (13),  $h = l \left(\frac{dv}{dp}\right)_T$ , hence, making use of the value of  $l$ , in equation (64),

$$h = T \frac{\delta^2 f}{\delta T \delta v} \bigg/ \left(\frac{d^2 f}{dv^2}\right)_T \quad . \quad . \quad . \quad (65)$$



The thermo-elastic coefficients can also be expressed in terms of  $f$  as follows: By definition  $\alpha_v = \frac{1}{p} \left( \frac{d p}{d T} \right)_v$ , hence, using the value of  $p$  in equation (57), we have

$$\alpha_v = \frac{\delta^2 f}{\delta v \delta T} \bigg/ \left( \frac{d f}{d v} \right)_T \quad . \quad . \quad . \quad (66)$$

Similarly the isothermal modulus of elasticity  $E_T = -v \left( \frac{d p}{d v} \right)_T$  by definition; but differentiating (57) with respect to  $v$ , keeping  $T$  constant, gives  $\left( \frac{d^2 f}{d v^2} \right)_T = - \left( \frac{d p}{d v} \right)_T$  and, substituting this in the defining equation for  $E_T$ , gives us

$$E_T = v \left( \frac{d^2 f}{d v^2} \right)_T \quad . \quad . \quad . \quad (67)$$

Also by equation (17),  $\alpha_p = \frac{\alpha_p E_T}{p}$ , hence, combining equations (66) and (67), and remembering that  $p = - \left( \frac{d F}{d V} \right)_T$ , we obtain

$$\alpha_p = - \frac{\delta^2 f}{\delta v \delta T} \left( \frac{d f}{d v} \right)_T \bigg/ \left( \frac{d f}{d v} \right)_T \frac{1}{v \left( \frac{d^2 f}{d v^2} \right)_T}$$

which reduces to

$$\alpha_p = - \frac{\delta^2 f}{\delta v \delta T} \bigg/ v \left( \frac{d^2 f}{d v^2} \right)_T \quad . \quad . \quad (68)$$

All these quantities can be expressed in terms of  $f'$  with equal ease, but the results will here be stated without proof.

$$C = T \left( \frac{d^2 f'}{d T^2} \right)_p \quad . \quad . \quad . \quad . \quad . \quad (69)$$

$$C - c = T \left( \frac{\delta^2 f'}{\delta T \delta p} \right)^2 \bigg/ \left( \frac{d^2 f'}{d p^2} \right)_T \quad . \quad . \quad (70)$$

$$h = -T \frac{\delta^2 f'}{\delta T \delta p} \quad . \quad . \quad . \quad . \quad (71)$$

$$l = T - \frac{\delta^2 f'}{\delta T \delta p} \bigg/ \left( \frac{d^2 f'}{d p^2} \right)_T \quad . \quad . \quad (72)$$

$$\alpha_v = - \frac{\delta^2 f'}{\delta p \delta T} \bigg/ p \left( \frac{d^2 f'}{d p^2} \right)_T \quad . \quad . \quad (73)$$

$$\alpha_p = \frac{\delta^2 f'}{\delta p \delta T} \bigg/ \left( \frac{d f'}{d p} \right)_T \quad . \quad . \quad . \quad (74)$$

$$E_T = - \left( \frac{d f'}{d p} \right)_T \bigg/ \left( \frac{d^2 f'}{d p^2} \right)_T \quad . \quad . \quad (75)$$

## CHAPTER V

### PERFECT GASES

**Joule's Law.**—We have so far assumed that the intrinsic energy,  $U$ , depended upon both the temperature and the internal molecular forces that vary with the state of a body, its volume, pressure, etc. If, however, the molecules are regarded as being so far apart that the influence they exert upon each other is negligibly small, their internal energy can be a function of the temperature only. This, of course, assumes that other forms of energy, such as chemical, do not enter into the thermodynamic discussion. We may, then, regard  $dU$  as having the form  $K dT$ , where  $K$  depends only upon the temperature. Such hypothetical bodies are known as “perfect gases,” and though no such gas exists, it is well known that all real gases at temperatures far removed from their critical points, such as hydrogen, helium, etc., at ordinary temperatures and pressures approximate very closely to the behavior of an ideal or perfect gas.

Making use of the fundamental postulate,  $dU = K dT$ , equation (27) becomes, for unit mass,  $dq = p dv + K dT$ , hence at constant volume,  $K = \left(\frac{dq}{dT}\right)_v$ . This derivative we have already called the specific heat at constant volume,  $c$ , which is thus shown to be a function of  $T$  only. Hence it follows that for unit mass of perfect gases,

$$d u = c d T, \quad . \quad . \quad . \quad (76)$$

and

$$d q = p d v + c d T. \quad . \quad . \quad . \quad (77)$$

But by equation (4),  $d q = c d T + l d v$ ; comparing this with (77) it is evident that in the case of perfect gases  $l = p$ , since they are coefficients of the same differential in similar equations.

Substituting this value of  $l$  in the equation of Clapeyron (42), we obtain its equivalent for ideal gases, or

$$l = p = T \left( \frac{d p}{d T} \right)_v \quad . \quad . \quad . \quad (78)$$

This may be written  $\left[ \frac{d p}{p} = \frac{d T}{T} \right]_v$ , which on integration

becomes  $\log p = \log T + \text{constant}$ , or in other words,  $p \propto T$ , when we assume that at the absolute zero a gas would exert no pressure, thus reducing the constant to 0. But this is the familiar law that at constant volume the pressure varies as the temperature, and is thus shown to depend upon our original assumption.

This postulate may be stated in another form, in which it is known as *Joule's law*, stating that *all the work done in compressing a gas at constant temperature is converted into heat*; or, conversely, that the work done by a gas expanding at constant temperature is all at the expense of the heat supplied by the system. It is evident that this is equivalent to saying that the intrinsic energy cannot vary either with the pressure or volume and so absorb heat or supply energy.

**Boyle's Law.**—The second fundamental postulate of perfect gases is Boyle's law, or  $[p v = \text{constant}]_T$ . If this is combined with the statement that  $[p \propto T]_v$ ,

which has just been shown to be a consequence of Joule's law, we find that  $p v \propto T$ , from which may be derived the law of Charles, or  $[v \propto T]_p$ . We may now make use of the familiar equation of perfect gases

$$p v = R T \quad . \quad . \quad . \quad . \quad (79)$$

which combines, in one expression, the two most important laws of perfect gases.

**Importance of Perfect Gases.**—The discussion of the properties of these imaginary bodies is of great value in the practical application of thermodynamics, for air and many other gases are sufficiently nearly "perfect" to justify our treating them as such, except in accurate observations and under high pressures, when the deviation may become very pronounced. Moreover, the equations relating to perfect gases are so much simpler and more easily derived than those of real gases, that it is well to develop them first, regarding them as limiting cases toward which real gases tend as they are removed from their critical temperatures; and then we may proceed, with their aid, to discuss the more difficult case of the real gases.

**Meaning of the Constant R.**—In making use of the equation  $p v = R T$ , it is well to understand the exact significance of the constant of proportionality  $R$ . If  $p$  expresses the pressure in kg. per sq. metre, and  $v$  is the volume of one kg. in cu. metres, then  $R$  has a definite value, but different for each gas. If it is known for one gas, it is readily found for all others by comparing their specific volumes at the same temperature and pressure, or

$$\left[ \frac{R_1}{R_2} = \frac{v_1}{v_2} \right]_{T, p}$$

But if, instead,  $v$  is taken as the volume occupied by a gramme-molecule of the gas, then, by Avogadro's principle, this volume will be the same for all gases at the same temperature and pressure, and  $R$  then becomes a universal constant for all gases, whose numerical value will depend only on the units chosen to express the three variables involved in the law. In what follows, unless otherwise stated,  $v$  will continue to stand for the specific volume, and  $R$  will, therefore, have a different value for each gas.

**Difference of the Specific Heats.**—By equation (48) we have  $C - c = T \frac{\delta v}{\delta T} \frac{\delta p}{\delta T}$ ; now from the partial differentiation of (79),  $p v = R T$ , we obtain  $\frac{\delta v}{\delta T} = \frac{R}{p}$  and  $\frac{\delta p}{\delta T} = \frac{R}{v}$ , substituting these values in (48), it becomes

$$C - c = T \left( \frac{R}{p} \right) \left( \frac{R}{v} \right) = \frac{T R^2}{p v} = \frac{T R^2}{R T} = R$$

The equation  $C - c = R$ , if we introduce the mechanical equivalent of heat at this point, and set  $A = \frac{1}{J}$ , becomes

$$C - c = R A \quad . \quad . \quad . \quad (80)$$

It shows that  $C - c$  is a constant for each gas, and since  $c$  can be a function of  $T$  only, the same must be true of  $C$ , while a knowledge of  $R$  and either of the specific heats enables us to determine the other. It does not follow, however, from the above proof, that  $C$  and  $c$  are individually independent of the temperature at which they are measured, but this is found by experiment to be very nearly the case for such gases as air, hydrogen, etc.; and we shall, therefore, add this third postulate concerning

perfect gases: that *the specific heats are constants independent of the temperature*. This is really Clausius' law, which states that the specific heat of a perfect gas at constant volume is independent of the temperature. From this it follows that  $C$  is constant, too, since  $C - c$  has already been shown to be independent of the temperature.

**Summary of Postulates.**—We have now seen that the the two fundamental assumptions with regard to perfect gases, or the laws of Joule and Boyle, give us, when combined, the familiar gas equation and all the ordinary properties of perfect gases. We further added Clausius' law which is not always included in the definition of a perfect gas, but which is really necessary in many calculations where we are forced to assume the specific heats constant. All three laws, while in a sense arbitrary, are justified by the tendency of gases toward approximate harmony with them, as they recede from their critical temperatures; and also by considerations based on the kinetic theory of gases, which would lead us to expect such laws in ideal bodies free from intermolecular forces or collisions.

**Determination of the Capacities.**— $\eta$ ,  $\lambda$  and  $h$ .—These quantities are readily found for the case of perfect gases by using equations (11), (12), and (13), in which each depends on a partial derivative and a heat capacity already determined. Thus, by (11),  $\eta = c \frac{\delta T}{\delta p}$ , but a partial differentiation of (79), gives  $\frac{\delta T}{\delta p} = \frac{v}{R}$ , hence we obtain

$$\eta = \frac{c v}{R} = \frac{c T}{p} \quad . \quad . \quad . \quad . \quad . \quad (81)$$

Similarly from (12),  $\lambda = C \frac{\delta T}{\delta v}$ , and  $\frac{\delta T}{\delta v} = \frac{p}{R}$  which follows by partial differentiation of (79), we have

$$\lambda = \frac{C p}{R} = \frac{C T}{v} \quad . \quad . \quad . \quad (82)$$

Using (13),  $h = l \frac{\delta v}{\delta p}$  and  $\frac{\delta v}{\delta p} = - \frac{R T}{p^2}$ , we find  $h = - \frac{l R T}{p^2}$ , but  $l = p$  for perfect gases, hence

$$h = - \frac{R T}{p} = - v \quad . \quad . \quad . \quad (83)$$

**Determination of U, S, F and F'.—**These functions are found as follows: Since  $dU$  is an exact differential, it is easy to integrate it between any assigned limits. Taking  $U_o$  as the potential of the gas at some arbitrarily chosen lower limit of temperature, and integrating

$\int_{U_o}^U dU = \int_{T_o}^T c dT$ , we have for unit mass

$$u = u_o + c (T - T_o) \quad . \quad . \quad . \quad (84)$$

Dividing (77) by  $T$  it becomes  $\frac{d q}{T} = d s = \frac{c}{T} d T + p \frac{d v}{T}$  which is an exact differential. Integrating between  $T$  and  $T_o$  we obtain

$$s = s_o + c \log \frac{T}{T_o} + R \log \frac{v}{v_o} \quad . \quad . \quad (85)$$

where  $s_o$  is the entropy at the arbitrarily chosen temperature  $T_o$  and corresponding volume  $v_o$ . To obtain  $F$ , take  $dF = dU - d(TS)$ , or, for unit volume,  $d f = d u - T d s - s_o d T$ . Integrating, and substituting for  $u - u_o$  from (84) and  $s - s_o$  from (85),

$$f - f_o = c (T - T_o) - T c \log \frac{T}{T_o} - T R \log \frac{v}{v_o} - s_o (T - T_o)$$



or

$$f = f_o + (c - s_o)(T - T_o) - T c \log \frac{T}{T_o} - T R \log \frac{v}{v_o} \quad (86)$$

Similarly  $dF' = d(U - TS + pV)$ , or for unit mass  $d f' = d(u - Ts + pv)$ , this may be integrated in the same manner, and becomes  $f' = f'_o + c(T - T_o)$

$$- s_o(T - T_o) - c T \log \frac{T}{T_o} - RT \log \frac{v}{v_o} + R(T - T_o).$$

But  $C - c = R$  and  $v = \frac{RT}{p}$ , hence, substituting these

$$\text{values, the above expression becomes } f' = f'_o + RT \log \frac{p}{p_o} - c T \log \frac{T}{T_o} + (C - s_o)(T - T_o) \quad (87)$$

(NOTE: We might, with equal ease, have determined  $F$  or  $F'$  before the heat capacities, and then have found  $h, l, C$ , etc., in terms of the potentials by equations (62) to (75). This method has many advantages, but the older way seems clearer and more convincing to the beginner in thermodynamics.)

**Thermoelastic Coefficients.**—These quantities, in the case of perfect gases, are obtained from the complete differential of (79), or  $p dv + v dp = R dT$ , dividing by  $p v = RT$ , we have  $\frac{dv}{v} = \frac{dT}{T} - \frac{dp}{p}$ , but by equation (14)  $\frac{dv}{v} = -\gamma_T dp + \alpha_p dT$ . From a comparison of

these equations, it is evident that  $\alpha_p = \frac{1}{T}$ , while  $\gamma_T = \frac{1}{p} = \frac{1}{E_T}$ , and  $\alpha_v$ , which is equal to  $\alpha_p \frac{E_T}{p}$ , reduces to  $\alpha_v = \frac{1}{T}$ , like  $\alpha_p$ .

We thus find that the two “coefficients of dilatation”

are each equal to the reciprocal of the temperature, while the modulus of elasticity at constant temperature is equal to the pressure, which is a well-known property of perfect gases.

**Determination of  $Q$  During a Transformation.**—Another important quantity is the amount of heat involved in any transformation of a perfect gas, expressed in terms of  $p$ ,  $v$ , and  $T$ . By equation (4),  $dq = c dT + l dv$ , and since for perfect gases,  $l = p$ , we may substitute  $l = p = \frac{RT}{v} = (C - c) \frac{T}{v}$

$$\therefore dq = c dT + (C - c) T \frac{dv}{v} \quad (88)$$

and since  $h = -v$ , we derive in an exactly similar manner,

$$dq = C dT - (C - c) T \frac{dp}{p} \quad (89)$$

Equations (88) and (89) are useful in calculating heat added at constant pressure or at constant volume.

Further if equation (77) is written in the form  $dq = c dT + A dw$ , it shows clearly that, in general, when we heat a perfect gas, a portion of the heat goes to raising the temperature, and the rest is consumed in doing external work. But if the heat is added isothermally, or  $dq = A dw$ , it is all converted into work, which is Joule's law, as has already been stated. If the gas expands adiabatically  $dq = 0$  and  $c dT = -A dw$ , or integrating between  $T_1$  and  $T_2$ ,  $c(T_1 - T_2) = u_1 - u_2 = -Aw$ , hence in this case it is clear that the work is done at the expense of the intrinsic energy of the gas.

**Adiabatic Transformations.**—The special case of an

adiabatic can be examined in more detail by aid of the general equation (2), or

$$dq = \lambda dv + \eta dp$$

Substituting (81),  $\eta = \frac{cT}{p}$ , and (82),  $\lambda = \frac{CT}{v}$

we obtain, for perfect gases:

$$dq = \frac{CTdv}{v} + \frac{cTdp}{p} \quad . \quad . \quad . \quad (90)$$

which is readily converted into an exact differential by dividing by  $T$ , giving

$$ds = \frac{Cdv}{v} + \frac{cdp}{p}$$

If the change is adiabatic,  $ds = 0$  and  $\frac{Cdv}{v} = -\frac{cdp}{p}$

Since  $C$  and  $c$  are constant for perfect gases, their ratio is also constant. This ratio which occurs constantly in dealing with gases will hereafter be designated by the letter  $\kappa$ , which is equal to  $\frac{C}{c}$ , and has a certain fixed value for each gas that is regarded as "perfect."

Dividing the last equation by  $c$  it may be written  $\kappa \frac{dv}{v} + \frac{dp}{p} = 0$ , on integrating, this exact differential becomes  $\kappa \log v + \log p = \text{constant}$ , which is readily transformed to

$$pv^\kappa = \text{constant, or } K, \quad . \quad . \quad . \quad (91)$$

which is the equation of the adiabatic curves of a perfect gas on the pressure-volume diagram. The numerical value of  $\kappa$  is 1.41 for air and most other diatomic gases or mixtures of such gases. Monatomic gases have a higher value, or about 1.67, while for such gases as  $\text{Cl}_2$ ,  $\text{Br}_2$  and

$I_2$ , which are partly dissociated at ordinary temperatures, the value of  $\kappa$  is about 1.30.

The constant of integration in equation (91) is readily found if the value of  $p$  is known for any arbitrarily chosen temperature. Suppose this temperature is  $0^\circ \text{C.}$ , then we have  $p_o v_o = R T_o$ , raising to the  $\kappa$ th power it becomes  $v_o^\kappa = \left(\frac{R T_o}{p_o}\right)^\kappa$ , or  $p_o v_o^\kappa = \frac{(R T_o)^\kappa}{p_o^{\kappa-1}}$ . But during an adiabatic transformation,  $p v^\kappa = p_o v_o^\kappa$

$$\therefore p v^\kappa = \frac{(R T_o)^\kappa}{p_o^{\kappa-1}} \quad . \quad . \quad . \quad . \quad (92)$$

which is the equation sought, in terms of known quantities.

**Isothermal Transformations.**—The case of isothermals is even simpler. Since  $p v = R T$ , if  $T$  is constant  $p v$  is constant, which shows that an isothermal plotted on the  $p v$  diagram is an equilateral hyperbola, and this curve is the graphic expression of Boyle's law.

**External Work During an Adiabatic Expansion.**—We have already seen that during an adiabatic change  $U_1 - U_2 = -A W$ , where  $A = \frac{1}{J}$  or, for unit mass and hydrostatic pressure

$$A w = A p (v_1 - v_2) = c (T_2 - T_1) \quad . \quad . \quad (93)$$

This may be expressed in terms of  $\kappa$  by virtue of the relation  $C - c = R A$ ; dividing by  $c$  we obtain  $\frac{C-c}{c} = \frac{R A}{c}$ , or  $\kappa - 1 = \frac{R A}{c}$  or

$$c = \frac{R A}{\kappa - 1} \quad . \quad . \quad . \quad . \quad (94)$$

hence

$$w = \frac{R(T_1 - T_2)}{\kappa - 1} \quad (95)$$

If we substitute  $p v = R T$ , (95) becomes  $w = \frac{p_1 v_1 - p_2 v_2}{\kappa - 1}$ ; and further, setting  $\frac{v_2}{v_1} = r$ , the ratio of expansion, and remembering that  $p_1 v_1^\kappa = p_2 v_2^\kappa$ , we obtain

$$w = \frac{p_1 v_1 (1 - r^{1-\kappa})}{\kappa - 1} \quad (95')$$

**Change of Temperature During an Adiabatic Expansion.**—It is frequently desirable to determine the change of temperature of a perfect gas for a given ratio between the final and initial volumes, during an adiabatic expansion. We have already seen (on page 82) that  $c dT = -A dw$  for an adiabatic change, or  $c dT = -A p dv$ , and dividing by  $p v = R T$ , we have  $A \frac{dv}{v} = -\frac{c dT}{R T}$ , which becomes, on integration:

$\log\left(\frac{v_1}{v_2}\right) = \frac{c}{RA} \log\left(\frac{T_2}{T_1}\right) = \frac{1}{\kappa - 1} \log\left(\frac{T_2}{T_1}\right)$ , which is readily transformed to

$$\frac{T_2}{T_1} = \left(\frac{1}{r}\right)^{\kappa-1} \quad (96)$$

where  $r = \frac{v_2}{v_1}$ , or the ratio of expansion.

The graphic significance of this equation is that any adiabatic, intersecting two given isothermals, cuts them at two points the ratio of whose volumes is constant. Or, in other words, any adiabatic expansion between the same two temperatures, involves the same ratio of expansion.

**External Work During an Isothermal Expansion.**—The work done during an isothermal expansion has been shown to be given by  $d q = A d w$ , or, if the pressure is hydrostatic,  $d w = p d v$ , but  $p = \frac{RT}{v}$ , hence  $d w = R T \frac{d v}{v}$ , where  $T$  is constant. Integrating between the limits of the final and initial volumes it becomes:

$$w = R T \log \frac{v_2}{v_1} = R T \log r$$

hence, during an isothermal expansion,

$$\begin{aligned} q &= A w = A R T \log r, \text{ or} \\ w &= R T \log r \end{aligned} \quad . \quad . \quad . \quad (97)$$

**External Work During any Closed Cycle.**—If a body is carried through a closed reversible cycle the integral of  $d U$  taken over the cycle is zero, just as it is for  $d S$ , both being exact differentials.

But for perfect gases and unit mass,  $d u = c d T$ ,  
 $\therefore \int c d T = 0$ , around any closed path. Integrating equation (77) with this in mind, it becomes  $q = A \int p d v$ , which shows that the external work done by a perfect gas carried through a closed cycle is at the expense of the heat  $Q$ , which must have been supplied to it from an external source.

**The Carnot Cycle Using a Perfect Gas.**—This cycle, though difficult to approximate experimentally, is extremely simple from a theoretical standpoint, and will therefore be considered before the cycles found more often in practice. Since, as we have just seen, the work

done during any cycle is at the expense of the heat supplied from without, and since no heat enters the gas during the two adiabatic changes,—it follows that the work done must be equivalent to the difference between the heat absorbed during the isothermal expansion, and

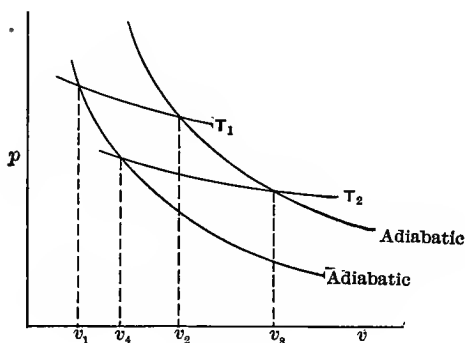


FIG. 15.

that rejected during the isothermal compression. We have shown that during an isothermal expansion  $q_1 = A R T_1 \log \left( \frac{v_2}{v_1} \right)$  (see p. 86) per unit mass of the working substance, where  $T_1$  is the temperature of the body and  $v_2$  and  $v_1$  its final and initial volumes respectively. Designating by  $v_3$  and  $v_4$  the initial and final volumes of the isothermal compression, and by  $T_2$  its temperature, the heat rejected to the refrigerator is  $q_2 = A R T_2 \log \frac{v_3}{v_4}$ . But it has already been pointed out that the ratio of volumes of any adiabatic intersecting two isotherms is a constant, hence, as will be evident from the diagram,  $\frac{v_2}{v_1} = \frac{v_3}{v_4} = r$ , therefore

$$q_1 - q_2 = A w = A R (T_1 - T_2) \log r \quad . \quad (98)$$

which gives the work per unit mass of the gas performing a Carnot cycle.

**Cycle of Constant Pressures and Constant Volumes.—**

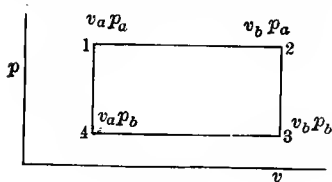


FIG. 16.

Another simple cycle of some practical interest is a rectangle on the  $p v$  diagram, as indicated in Fig. 16. As before, the total external work is equal to the difference

between the heat received and that rejected during the cycle, or  $\int dQ = A \int dW$ . Take equation (88), and eliminate  $T$  by the relation  $T = \frac{p v}{R}$ , and we obtain:

$$d q = \frac{c v d p}{R} + \frac{C p d v}{R}$$

There are four steps to be considered. First, keeping  $p$  constant, the above equation becomes:

$$q_{1, 2} = \frac{C p_a}{R} (v_a - v_b)$$

next, keeping  $v$  constant,

$$q_{2, 3} = \frac{c v_b}{R} (p_a - p_b)$$

third, keeping  $p$  constant,

$$q_{3, 4} = \frac{C p_b}{R} (v_b - v_a)$$

fourth, keeping  $v$  constant,

$$q_{4, 1} = \frac{c v_a}{R} (p_b - p_a)$$



Taking the sum of the steps, we obtain,

$$\Sigma q = \frac{C}{R} (p_b - p_a) (v_b - v_a) - \frac{c}{R} (v_b - v_a) (p_b - p_a)$$

or,

$$\Sigma q = \frac{C-c}{R} \Delta p \Delta v = A \Delta p \Delta v,$$

which conclusion could readily have been predicted.

**The "Stirling Cycle."**—A less simple cycle, but one that has been approximated in practice in a certain type of hot-air engine, is bounded by lines of constant volume and constant temperature. Here again equation (88) may be used if we substitute  $p = \frac{RT}{v}$  and multiply by  $A$  to reduce to heat units, giving  $dq = c dT + AR T \frac{dv}{v}$ .

During the first isometric change, from  $A$  to  $B$  (see Fig. 17, p. 90),  $v$  is constant and  $dv = 0$ ; hence :

$$\begin{aligned} \int dq_{AB} &= c \int_{T_2}^{T_1} dT, \text{ similarly} \\ \int dq_{BC} &= AR T_1 \int_{v_1}^{v_2} \frac{dv}{v}, \text{ because } T = \text{const} \\ \int dq_{CD} &= c \int_{T_1}^{T_2} dT \\ \int dq_{DA} &= AR T_2 \int_{v_2}^{v_1} \frac{dv}{v} \end{aligned}$$

$$\therefore \Sigma q = (C - c) (T_1 - T_2) \log r$$

$$\therefore \Sigma q = A w = R (T_1 - T_2) \log r$$

which is the same expression as that derived in the case of Carnot's cycle. This was to be expected, however,

from Carnot's principle, by which all reversible engines working between the same temperature limits have the same efficiency, and if we assign the same value of  $r$  to

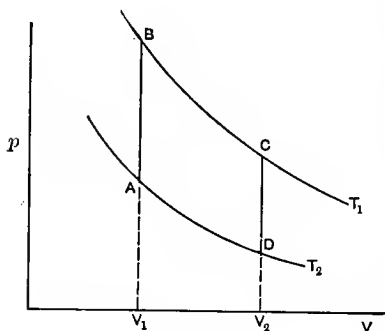


FIG. 17.

the two cycles, the same quantity of heat will be absorbed, and consequently the same external work performed.

### Experimental Determination of C.—

The actual measurement of the specific heat of a gas, approximating at all closely

to a perfect gas, is most difficult owing to the low density of such bodies at the temperatures and pressures at which they must necessarily be measured, in order that they may be sufficiently removed from the critical point.

The specific heat at constant pressure is more readily measured than that at constant volume, and if  $C$  is known,  $c$  may be found either from  $A = \frac{C-c}{R}$ , or  $\frac{C}{c} = \kappa$ , provided  $R$  or  $\kappa$  are known for the gas in question.

The method used for finding  $C$  is to pass the gas from a receiver through a heating coil, and then into a calorimeter consisting of a "worm" immersed in water. The flow is made very slow, so that the pressure throughout the calorimeter is sensibly the same, and constant during the run. The specific heat is then calculated from

$$\text{the equation: } MC \left( T - \frac{T_o + T_1}{2} \right) = M' (T - T_o),$$

where  $M$  is the amount of gas that has passed through the calorimeter,  $T$  is its initial temperature,  $T_0$  and  $T_1$  are the initial and final temperatures of the water, and  $M'$  is the mass of the water and the "water equivalent" of the calorimeter. In this equation it is assumed that there is no loss of heat from the water, and that the temperature rises uniformly from start to finish. This will approximately be realized if  $T$  is much larger than both  $T_0$  and  $T_1$ . The value of  $C$  for air is 0.23. It is found to be practically independent of the temperature and pressure, thus agreeing with our assumption that at ordinary temperatures and pressures air behaves like a nearly perfect gas.

**Experimental Determination of  $\kappa$ .**—The ratio of the specific heats of a gas that is assumed to be perfect is best determined by measuring the velocity of sound through that gas. This velocity is shown to depend upon  $\kappa$  as follows: Newton proved that the velocity of a longitudinal wave through an elastic medium is given by  $u = \sqrt{\frac{E}{\rho}}$ , where  $u$  is the velocity,  $E$  is the modulus of elasticity and  $\rho$  is the density of the medium. It was found that this equation gave satisfactory results for solids and liquids. In the case of gases, Newton modified it by substituting the pressure for  $E$ . This equality was derived on (p. 81), where it was found that for a perfect gas  $E_T = p$ ; hence, in making this substitution, Newton assumed the temperature to be constant during the passage of the wave. Using the formula  $u = \sqrt{\frac{p}{\rho}}$  gives a result that is more than 15 per cent too low. The error is due to assuming the

temperature constant and using the isothermal modulus. Instead, the adiabatic modulus  $E_s$  should be employed, for the compressions and rarefactions do produce heatings and coolings which are, however, of such short duration that they may be considered as strictly adiabatic. But we have already proved, see (17'), that  $E_s = \kappa E_T$ , therefore

$$E_s = \kappa p \quad . \quad . \quad . \quad . \quad (99)$$

and the true expression for the velocity of sound in a gas is

$$u = \sqrt{\frac{\kappa p}{\rho}} \quad . \quad . \quad . \quad . \quad (100)$$

which gives the velocity approximately as determined by direct experiment. This is known as Laplace's formula and it is applicable to all supposedly perfect gases; but Newton's formula is used in the case of liquids and solids, because the compressions and expansions are too small to produce any appreciable change in temperature and the modulus of elasticity may be taken as  $E_T$ . In fact no other modulus is ordinarily considered, and we write simply  $E$ . In actual experiment, it is usual to reduce the readings to  $0^\circ$  C., by the modified form of Laplace's equation,

$$u_0 = \sqrt{\frac{\kappa p}{\rho_0} (1 + 0.003665 t)}$$

where  $p$  is the observed pressure and  $\rho_0$  the density at  $0^\circ$  C. of the gas in question. The apparatus used is some form of Kundt's tube, as described in all elementary treatises on sound.

**Method of Clément and Desormes.**—A totally different and much less accurate method for determining  $\kappa$

was used by Clément and Desormes in 1819. It is interesting historically, however, and is a good illustration of some of the principles of perfect gases. A large receiver  $R$  having an ample neck is fitted with a stopcock  $S$ , so that  $R$  may be easily and rapidly thrown

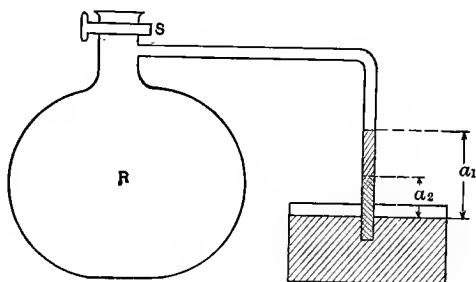


FIG. 18.

into free communication with the atmosphere. A side tube of small diameter connecting with  $R$ , as shown, is arranged to dip under the surface of some colored liquid whose density  $\rho$  is known, and is thus a manometer capable of indicating the pressure in  $R$  over a small range, less than the atmosphere.

The receiver is to be partially exhausted until the liquid in the manometer rises to a height  $a_1$ ; then close  $S$  and allow sufficient time to establish equilibrium between the temperatures within and without the receiver. Now open  $S$ , allowing the liquid in the tube to sink to 0, and instantly close  $S$  again. If this process is sufficiently rapid, and if the receiver is large enough, we may assume that the compression caused by the in-rushing air was adiabatic, since there was no time for the heat generated to escape, and the air in the vessel

is thus warmer than the surrounding atmosphere. The increase in pressure is  $\Delta p_1 = a_1 \rho g$ . After the stop-cock is closed again a much slower change takes place. The air in  $R$  cools down to the temperature outside, and the manometer indicates a slow fall in pressure until it stands at a new level  $a_2$ , which indicates a pressure change  $\Delta p_2 = a_2 \rho g$ . This latter change is sensibly at constant volume, since the bore of the tube is small compared to  $R$ . During the first, or adiabatic change,  $d q = 0$ , hence, by equation (3),

$$\left[ d p = -\frac{C d T}{h} \right]_s$$

During the second change, when  $v$  is constant, by equation (7),

$$\left[ d p = -\frac{(C-c)}{h} d T \right]_v$$

hence for the finite changes observed, we have

$$\Delta p_1 = a_1 \rho g = -\frac{C}{h} \Delta T_1 \quad . \quad . \quad . \quad (i)$$

and

$$\Delta p_2 = a_2 \rho g = -\frac{(C-c) \Delta T_2}{h} \quad . \quad . \quad (ii)$$

But  $\Delta T_1 = \Delta T_2$  since the vessel ultimately returns to its original temperature, therefore, dividing (i) by (ii), we obtain

$$\frac{a_1}{a_2} = \frac{C}{C-c}$$

$$\text{or } \frac{C}{c} = \kappa = \frac{a_1}{a_1 - a_2}$$

This method is open to serious experimental difficulties, some of which are noted in Preston's "Theory of Heat"

(p. 291). But it has been repeated by numerous observers who have partially eliminated these errors. In the more recent attempts it has been found better to compress the air in  $R$  rather than to exhaust it (see Poynting,\* p. 292), and the values of  $\kappa$  thus obtained agree excellently with those found from the velocity of sound.

**Rate of Flow of Gases Under Pressure.**—An important application of the laws of perfect gases is the consideration of the flow of such gases through tubes under

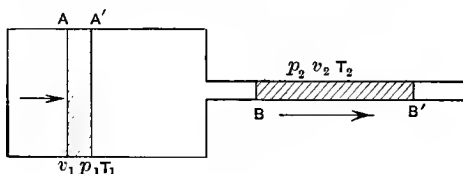


FIG. 19.

pressure. Suppose the surface of a piston moving in the large cylinder as shown in Fig. 19, is advanced from  $A$  to  $A'$  so as to displace a unit mass of the gas, and suppose a section of the gas in the tube advances, in consequence, from  $B$  to  $B'$  with a velocity  $u$ . Let  $v_1$  be the volume swept out by the piston (*i.e.*, the specific volume of the gas in the cylinder), and let  $v_2$  be the volume swept out by the advancing section in the tube, between  $B$  and  $B'$ . Let  $p_1$  and  $p_2$  be the pressures in the two volumes considered where  $p_1 > p_2$  as long as the piston is moving. Further let  $T_1$  equal the temperature of the gas after undergoing compression and  $T_2$  the temperature after expansion, or the temperature of the undisturbed gas. If the piston moves at a uniform rate, then  $p_1$  is constant, and the mechanical work done

\* "A Text-Book of Physics, Heat"; Poynting and Thomson, published by Lippincott.

by the piston in sweeping out the volume we are considering is equal to  $p_1 v_1 = R \int_{T_2}^{T_1} dT$ , or  $p_1 v_1 = R(T_1 - T_2)$ . But this work done on the gas in the cylinder results in two effects in the gas in the tube. Owing to the small section of the tube, the unit mass of gas will acquire a kinetic energy equal to  $\frac{1}{2}u^2$ , an effect which was negligible in the slowly moving gas in the cylinder; moreover the gas in the tube expands back to its original pressure, and so loses temperature or intrinsic energy; hence the work done on the gas,  $p_1 v_1 = R(T_1 - T_2) = \frac{1}{2}u^2 - c J (T_1 - T_2)$ . Substituting  $R = J(C - c)$ , this equation becomes

$$\frac{1}{2}u^2 = J C (T_1 - T_2) \quad . \quad . \quad (101)$$

This expression, for the velocity, may be transformed to depend upon the *pressures*, which are more easily measured than the temperatures. If the expansion is sufficiently rapid it may be regarded as adiabatic, hence we may use equation (96), or

$$\frac{T_2}{T_1} = \left( \frac{v_1}{v_2} \right)^{\kappa - 1}$$

this is readily transformed to

$$\frac{T_2}{T_1} = \left( \frac{p_2}{p_1} \right)^{\frac{\kappa - 1}{\kappa}} \quad . \quad . \quad . \quad (102)$$

by substituting  $\frac{v_1}{v_2} = \left( \frac{p_2}{p_1} \right)^{\frac{1}{\kappa}}$ , which follows from equation (91). Substituting (102) in (101), we obtain,

$$u = \sqrt{2 C T_1 J (p_1^{\frac{\kappa - 1}{\kappa}} - p_2^{\frac{\kappa - 1}{\kappa}}) / p_1^{\frac{\kappa - 1}{\kappa}}}. \quad (103)$$



in which the velocity is expressed in terms of the initial temperature, and the two pressures.

**Expansion Into a Vacuum.**—If the gas expands into a perfect vacuum  $p_2 = 0$ . (103) reduces to

$$u^2 = 2 C T_1 J \quad . \quad . \quad . \quad (104)$$

This gives the highest attainable velocity of a compressed gas at any given temperature  $T_1$ . In the case of ordinary atmospheric air under the usual conditions of temperature and pressure, this velocity is about 800 metres per second. It is interesting to note that this velocity depends upon the specific heat at constant pressure, rather than the specific heat at constant volume. Thus it is clear that the kinetic energy developed is at the expense of both the thermal and mechanical energy due to compression; for if it depended on  $c$  it would be due to the thermal, or intrinsic energy only, as has already been explained; while a purely mechanical storing up of energy in the compressed gas would be at constant temperature and therefore proportional to  $R$ , or  $C - c$ .

**Height of the Atmosphere.**—The height of the earth's atmosphere can be roughly determined by means of the laws of perfect gases. Suppose the various horizontal strata of the atmosphere are in absolute thermal equilibrium, so that there is no flow of heat from one to the other; then  $T$  at any given height is constant, and since there is no transfer of heat, we may regard the state as adiabatic.

Also suppose the acceleration due to gravity,  $g$ , constant and independent of the altitude. Let  $\rho$  = the density at any altitude, let  $h$  be the height, and  $p$  and  $v$  the pressure and specific volume, then



familiar principle of Torricelli. Hence  $\frac{1}{2}u^2 = g H$ , but  $\frac{1}{2}u^2 = J C T_1$  by equation (104)  $\therefore H = \frac{J C T_1}{g}$ , as above. This value of  $H$  is about 27 kilometres and the temperature gradient thus indicated is approximately  $1^\circ$  for 100 metres, which is substantially true near the surface of the earth.

**Barometric Measurement of Altitudes.**—The determination of altitudes by means of the barometer is usually based on the assumption that the atmosphere is isothermal, rather than adiabatic. Therefore, assuming  $T$  constant, the height of the so-called “homogeneous atmosphere,”  $H'$ , is constant, for by definition  $H' = \frac{p}{\rho g}$ , but

$$\frac{p}{\rho g} = \frac{p v}{g} = \frac{p_o v_o}{g} = \frac{R T_o}{g} = \text{constant.}$$

Substituting  $\frac{p}{H'}$  for  $\rho g$  in the equation  $-d p = \rho g d h$ , we obtain  $d h = -H' \frac{d p}{p}$ ; then integrating between  $o$  and  $h$ , and substituting  $\frac{R T_o}{g}$  for  $H'$

$$h = \frac{R T_o}{g} \log \frac{p_o}{p} \quad . \quad . \quad . \quad (106)$$

where  $p_o$  and  $T_o$  are the pressure and temperature at sea level.

But it is also possible to calculate  $h$  on the assumption of an adiabatic atmosphere, as in the last paragraph. In this case  $p v^\kappa = K$ ; therefore eliminating  $v$  from  $-v d p = g d h$ , we obtain

$$d h = - \frac{K^{\frac{1}{\kappa}}}{g} \frac{d p}{p^{\frac{1}{\kappa}}}$$

Integrating as before

$$h = \frac{K^{\frac{1}{\kappa}}}{g(\kappa-1)} \left( p_o^{\frac{\kappa-1}{\kappa}} - p^{\frac{\kappa-1}{\kappa}} \right)$$

and substituting the value of  $K$  given in (92)

$$h = \frac{R T_o \kappa}{g(\kappa-1)} \left( 1 - \left( \frac{p}{p_o} \right)^{\frac{\kappa-1}{\kappa}} \right) \quad (106')$$

where  $h$  may be computed if the pressure and temperature at sea level have been observed simultaneously with the pressure at  $h$ .

This method of calculating  $h$  is much more accurate at great altitudes than the former, as may be seen by setting  $p = 0$  in (106), which makes  $h$  infinite; while, if  $p = 0$  in (106'),  $h$  becomes  $\frac{R T_o \kappa}{g(\kappa-1)}$ ; but by (94)  $R = J(\kappa-1)c$ , or  $R = \frac{J(\kappa-1)C}{\kappa}$ ; hence, substituting for  $R$ ,  $h = \frac{J C T_o}{g}$ , which is the height of the adiabatic atmosphere as proved in the preceding paragraph.

## CHAPTER VI

### REAL GASES

IN the last chapter we considered the behavior of bodies whose internal energy varied with the temperature only. This amounts to tacitly ignoring the intermolecular actions that may exist even in the case of the most nearly perfect gases. In the case of such gases as hydrogen and oxygen, however, such an assumption leads to no very serious error at ordinary temperatures and pressures, but if we examine the behavior of carbon dioxide, or any other gas whose critical temperature and pressure are not too far below the ordinary temperature and pressure of the atmosphere, or if we subject even hydrogen to a very low temperature and high pressure, the assumption that they behave as perfect gases gives results very far removed from the experimental facts, and we should be wholly wrong in treating them as the ideal bodies assumed in the last chapter.

In such cases the deviations from the laws of Boyle, Charles, and Clausius are very marked, and we are forced at once to abandon the simpler relation  $p v = R T$  and look for an equivalent expression that may give a closer approximation to the actual facts as determined by experiment. Moreover, the specific heats may no longer be regarded as independent of the temperature, and new expressions for  $C$  and  $c$ , as well as for all the other thermal capacities, must be found.

**Possibility of Accurately Expressing the Laws of a Real Gas.**—Various attempts have been made to express the relation between  $p$ ,  $v$  and  $T$  in an equation that will hold under all possible conditions of a gas; but none have so far proved absolutely accurate, and it is probable that the relations involved are so complex that no perfect solution will ever be achieved. In fact Kamerlingh Onnes, of Leyden, has practically admitted this by abandoning finite equations, and making use of an infinite series in negative powers of  $v$  in order to express the long-sought relation.

But we shall here discuss two earlier partial solutions of the problem, whose comparative simplicity makes them available for numerical calculations, and they yield results that are remarkably accurate within certain ranges to which each equation seems peculiarly adapted.

Practically all proposed solutions of this problem, till that of Onnes, have been of the general form

$$(p + \pi)(v - \phi) = RT,$$

where a certain function  $\pi$  is to be added to the pressure, and a certain other function  $\phi$  must be subtracted from the volume. The function  $\pi$  may involve both volume and temperature, while  $\phi$  is a function of the volume only. The various solutions, however, differ as to the exact nature of these functions. The addition to  $p$  is necessary because of the intermolecular attractions, and the diminution of  $v$  because of the effective reduction of the volume of the gas by the volume of the molecules themselves, thus involving collisions between them.

**Van der Waals' Equation.**—This solution is the most celebrated of any, and perhaps the simplest, although

it is not the most accurate. It has one great advantage over the others in that the meaning of the constants introduced is fairly apparent. Van der Waals assumed that:

$$\left(p + \frac{a}{v^2}\right)(v - b) = R T. \quad . \quad . \quad (107)$$

in which  $R$  has the same value as in the simpler equation for perfect gases, and  $a$  and  $b$  are constants dependent upon the nature of the gas. It will be noticed at once that the specific volume  $v$  has been reduced by a constant volume  $b$  which, as was said above, depends upon the volume of the molecules. In fact  $b$  is called the co-volume, and is the least possible space occupied by the molecules if they are crowded together. If the volume occupied by a gramme of the gas becomes equal to this co-volume, then  $v = b$  and  $T = 0$ . In other words, this crowding would only occur if the temperature were reduced to the absolute zero, and the agitation of the molecules ceased altogether.

The quantity  $a/v^2$  must obviously be in the nature of a pressure, or intensity of a force, and the constant  $a$  determines the amount of this force which varies inversely as the square of the specific volume. The reason for this is apparent if we consider that the attraction between any two portions of a gas must vary as the number of particles in each, and therefore varies as the product of the two densities. But the density is constant throughout a small body of gas in equilibrium, hence the attraction must vary as the density squared, or inversely as the square of the specific volume. This quantity,  $a/v^2$ , obviously tends to diminish the pressure due to the bombardment of the molecules on the walls

of a containing vessel, hence it must be added to  $p$  in order to obtain the true internal pressure of the gas. Further it should be noticed that in the case of a very "light" gas like hydrogen,  $v$  is very large, and this correction is insignificant, but it increases in importance as  $v$  diminishes.

**Plotting Van der Waals' Equation.**—The graphic form and properties of Van der Waals' equation may be investigated by a very simple analysis. If the equation is solved for  $p$ , it becomes

$$p = -\frac{a}{v^2} + \frac{RT}{v-b}. \quad \dots \quad (108)$$

Now set  $-a/v^2 = p_1$  and  $RT/(v-b) = p_2$ . Then plot two isothermal curves for  $p_1$  and  $p_2$  using vol-

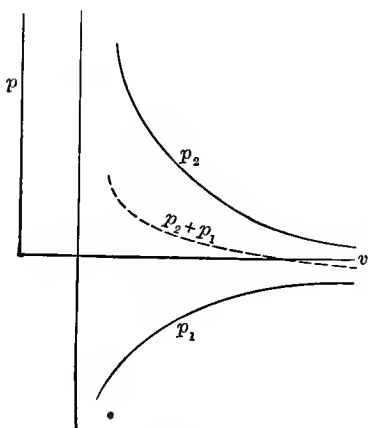


FIG. 20.

umes as abscissæ. A third curve whose ordinates are the sum of the ordinates of the last two, or  $p_1 + p_2$ , plotted as a function of  $v$ , expresses the relation between  $p$  and  $v$  in Van der Waals' equation, assuming the temperature constant. This is shown in Fig. 20, where the dotted curve gives this relation for an arbitrarily

assumed value of  $T$  over a small range of volumes. The particular case represented applies to a very low tem-



perature (*i.e.*, far below the critical temperature of the gas). Here it will be seen that for rather large specific volumes the pressure becomes negative, which means that there exists a tension in the body. This apparently

anomalous conclusion can be experimentally realized in the liquid state (and Van der Waals' equation is intended to cover both the liquid and gaseous states at low temperatures). Prof. Bouty of the University of Paris, by carefully expelling all trace of air, has succeeded in producing a tension of half an atmosphere in a column

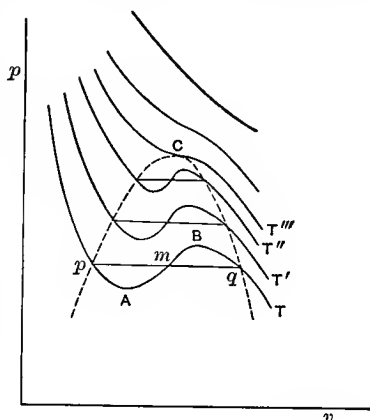


FIG. 21.

of water, and nearly one atmosphere in a column of mercury. At temperatures, however, not too far below the critical, the curve obtained by plotting  $p_1 + p_2$  takes the familiar form shown in Fig. 21.

**Experimental Verification.**—Experiment only partially justifies the peculiar form of Van der Waals' curve at temperatures below the critical value. In ordinary observations the isothermal goes directly from  $p$  to  $q$ , as indicated by the dotted line, and does not follow the curved path of the equation, thus producing two points of discontinuity. Now it is natural to regard discontinuity in curves that express some fundamental relation as more or less accidental, even if the accident almost

universally happens. In point of fact we may so regard the points  $p$  and  $q$ . It is evident that at the point  $p$  begins a sudden increase in volume while the pressure remains constant, which indicates the sudden vaporization that occurs when the pressure on a liquid is sufficiently reduced. This will continue at constant pressure until all the liquid is vaporized at  $q$ . From there on, the vapor continues to expand, as the pressure is further reduced, following a continuous curve. Now, if the pressure is lowered over a liquid under certain very special conditions, we can carry the curve without discontinuity nearly to the point  $A$ . Similarly a vapor free from dust or other condensation nuclei may be supersaturated nearly up to the point  $B$ . If, however, we attempt to pass beyond  $A$  or  $B$  there will be an explosive transformation involving either a sudden and complete vaporization, or an equally abrupt condensation, because the portion of the curve between  $A$  and  $B$  is essentially unstable, representing as it does the anomalous condition of the volume and pressure increasing simultaneously.

It may be that the substance really does follow the curved path, although the change is so rapid that it cannot be detected. Since condensation nuclei or dust particles may be regarded as accidents in a liquid or vapor, we are justified in considering a continuous curve like that of Van der Waals as an approximate representation of the ideal transformation from liquid to vapor, or vice versa.

**Singular Points in the Curve.**—In order to locate the points  $A$  and  $B$ , differentiate the original equation, solved for  $p$ , giving

$$\frac{d p}{d v} = \frac{2 a}{v^3} - \frac{R T}{(v-b)^2}$$

setting this equal to zero to obtain a maximum or minimum,

$$\frac{2 a}{v^3} = \frac{R T}{(v-b)^2} \quad . \quad . \quad . \quad (109)$$

A solution of this equation would locate  $A$  and  $B$  on any isothermal. The points of discontinuity  $p$  and  $q$  may be found graphically as follows: It was proved

on (p. 52) that the external work involved in carrying a body through an isothermal cycle is zero, hence, since the shaded areas indicate work, and if we consider the isothermal cycle  $p A c B q c p$ , it

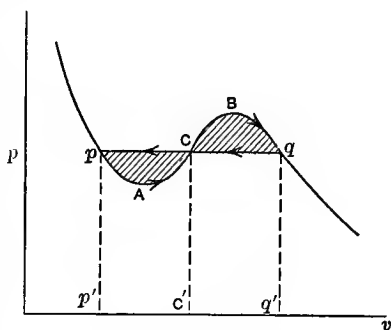


FIG. 22.

follows that the area  $(p' p A c B q q' - p' p q q') = 0$ , since this is proportional to the work done during the cycle. Expanding this relation, we obtain,

$$p' p A c c' + c' c B q q' - p' p c c' - c' c q q' = 0.$$

But  $p' p A c c' - p' p c c' = -p A c$ , and  $c' c B q q' - c' c q q' = +c B q$ .  $\therefore c B q - p A c = 0$ , hence the areas of the two shaded loops are equal. Therefore, to find  $p$  and  $q$ , lay off a horizontal line  $p q$ , so that the two intercepted areas are equal, and the intersection of this line with the curve determines  $p$ ,  $q$  and  $c$ .

Between  $A$  and  $B$  there is a point of inflection (not

necessarily at  $c$ ) which is found by setting the second derivative  $d^2 p/dv^2 = 0$ , which gives

$$\frac{-6a}{v^4} + \frac{2RT}{(v-b)^3} = 0. \quad (110)$$

A solution of this equation would locate  $m$  (Fig. 21), which is supposed to be this singular point.

**Critical Point.**—There is a certain isothermal, as indicated in Fig. 21, where the two loops vanish at  $C$ , thus indicating two equal real roots of equation (109). But equation (110), where  $d^2 p/dv^2 = 0$ , also applies at this point, and a combination of them both makes it possible to determine the values of the pressure, volume, and temperature at the critical point  $C$ . The solution for  $v$  then follows by eliminating  $RT$  between (109) and (110), and there results

$$v_c = 3b, \quad (110')$$

where  $v_c$  is the critical volume.

Substituting this value of  $v$  in (109), gives:

$$T_c = \frac{8a}{27bR} \quad (110'')$$

where  $T_c$  is the temperature of the isothermal passing through  $C$ , or simply the critical temperature. Introducing these values of the critical volume and critical temperature in the original equation of Van der Waals (107), it becomes

$$p_c = \frac{a}{27b^2} \quad (110''')$$

where  $p_c$  is the critical pressure.

**Comparison with Perfect Gases.**—If we eliminate  $a$  and  $b$ , by aid of these values of the critical volume, temperature, and pressure, Van der Waals' equation'

reduces to the very simple form

$$p_c v_c = \frac{3}{8} R T_c \quad . \quad . \quad . \quad (111)$$

Comparing this with  $p v = R T$ , it is evident that the critical volume is  $\frac{3}{8}$  of the value that would be called for, if  $p v = R T$  were true at the critical temperature; hence the critical density is 2.67 times larger than for a perfect gas. It is found that in case of such diatomic gases as  $N_2$  and  $O_2$ , the ratio is 3.8, while in the case of more complex gases it is even higher; methane, for instance, having a density 3.85 times too great for a perfect gas, at its critical temperature. But in the case of the monatomic gases this ratio closely approximates the theoretical value, being, for instance, 2.71 in the case of argon. This would seem to indicate that assuming the co-volume  $b$  to be a constant is only admissible for monatomic gases.

**Law of Corresponding States.**—We have just seen that Van der Waals' equation may be expressed in terms of the critical values of the temperature, volume, and pressure of the gas considered, hence if we measure the three variables in terms of their critical values, we shall rid the equation of quantities that depend upon that particular gas, and so render it applicable to all gases. Therefore let  $P = \frac{p}{p_c}$ ,  $\theta = \frac{T}{T_c}$  and  $V = \frac{v}{v_c}$ , then  $p = \frac{P a}{27 b^2}$ ,  $T = \frac{8 a \theta}{27 b R}$ , and  $v = 3 V b$ . Substituting these values in Van der Waals' equation, it reduces to the remarkable form

$$\left(P + \frac{3}{V^2}\right)(3V - 1) = 8\theta \quad . \quad . \quad (112)$$

This is a unique expression applicable to all gases,

though it involves different units of measure for each gas. Thus if a series of isothermals is plotted, as in Fig. 21, for a particular gas, using any scale for  $p$  and  $v$ , a similar series representing any other gas may be made exactly to coincide with the former set, by properly extending or reducing the  $p$  and  $v$  scales. This is known as the theorem of "corresponding states," because, according to the theorem, two gases, whose  $p v$  and  $T$  are numerically the same when measured in terms of the critical values of those quantities, are physically in an exactly equivalent condition. It should be observed, however, that this theorem can only be proved when there are not more than three constants in the defining equation. If there are four constants or more, it is obviously impossible to eliminate them all by choosing some particular scale for the three variables. We can, therefore, only regard this theorem as a very interesting property of a Van der Waals body, but not exactly in conformity with the facts, any more than Van der Waals' equation exactly describes any real gas.

**Various Properties of a Van der Waals Body.**—Equation (107) is readily solved for  $p$ , as in (108), but it is a cubic in  $v$ , having three roots, all of them real over a small range of pressure. Outside this range two are imaginary, which is evident from the form of the curve; hence many of the functions which are readily found for perfect gases can only be expressed symbolically for a Van der Waals body.

If, however, we set  $v = f(p, T)$  as a symbolic solution of the equation, and  $\frac{\delta v}{\delta T} = f', (p, T)_p$ , also  $\frac{\delta v}{\delta p} = f''(p, T)_T$ , we may still derive some very interesting relations.

In what follows we shall use the method, already suggested, of determining the potential and entropy first, and then deriving the heat capacities, by means of the relations established between the potentials and those capacities.

**Entropy.**—Solving Van der Waals' equation for  $p$  and differentiating with respect to  $T$ , keeping  $v$  constant, gives  $T \frac{\delta p}{\delta T} = \frac{RT}{v-b}$ . But by equations (4) and (42)

$$d q = c d T + T \frac{\delta p}{\delta T} d v . \quad . \quad . \quad (i)$$

substituting for  $\frac{\delta p}{\delta T}$  gives

$$d q = c d T + R T \frac{d v}{v-b} . \quad . \quad . \quad (ii)$$

$$\text{but } d s = \frac{d q}{T} = \frac{c d T}{T} + \frac{R d v}{v-b} . \quad . \quad . \quad (iii)$$

Integrating, we obtain the entropy measured from any arbitrary value  $s_o$ , or

$$s = s_o + c \log \frac{T}{T_o} + R \log \left( \frac{v-b}{v_o-b} \right) . \quad (113)$$

**Intrinsic Energy.**—By definition  $d U = d Q - p d V$ , hence, making use of equation (ii) in the last paragraph, we have, for unit mass

$$\begin{aligned} d u &= c d T + \frac{R T d v}{v-b} - p d v \\ \therefore d u &= c d T + \left( \frac{R T}{v-b} - p \right) d v \\ &= c d T + \left( \frac{R T}{v-b} + \frac{a}{v^2} - \frac{R T}{v-b} \right) d v \\ &= c d T + \frac{a}{v^2} d v . \quad . \quad . \quad (i) \end{aligned}$$

$$\text{hence } u = u_o + c (T - T_o) - \left(\frac{a}{v}\right)_{v_o}^v$$

$$u = u_o + c (T - T_o) + a \left( \frac{v - v_o}{v v_o} \right) \quad . \quad (114)$$

where  $u_o$ ,  $v_o$  and  $T_o$  are the values at any arbitrarily chosen state.

From equation (114) it is evident that when a Van der Waals body is heated its intrinsic energy increases from two sources, one being the rise of temperature and the other the change in volume. This latter effect is necessary from the properties we have supposed such bodies to possess, but it does not exist in the case of perfect gases, where temperature alone alters the intrinsic energy.

**Potential, F.**—Again, by definition  $dF = dU - d(TS)$ , or for unit mass  $df = du - T ds - s_o dT$ . Using the values for  $ds$  and  $du$  above, we have

$$df = \frac{a}{v^2} dv - \frac{TR dv}{v-b} - s_o dT \quad . \quad . \quad (i)$$

integrating,

$$f = f_o + (c - s_o)(T - T_o) - Tc \log \frac{T}{T_o} - RT \log \left( \frac{v-b}{v_o-b} \right) + a \left( \frac{v-v_o}{v v_o} \right) \quad (115)$$

**Thermal Capacities.**—By equation (64)  $l = -T \frac{\delta^2 f}{\delta T \delta v}$  but from (i) above we derive  $\left( \frac{df}{dv} \right)_T = \frac{a}{v^2} - \frac{TR}{v-b}$

$$\therefore l = \frac{TR}{v-b} = p + \frac{a}{v^2} \quad . \quad . \quad (116)$$



Similarly  $h = T \left( \frac{\delta^2 f}{\delta T \delta v} \right) / \left( \frac{d^2 f}{d v^2} \right)_T$  by equation (65),

$$\begin{aligned} h &= \frac{- \left( p + \frac{a}{v^2} \right)}{\frac{- 2 a (v-b)^2 - R T v^3}{v^3 (v-b)^2}} \\ \therefore h &= \frac{R T \left( \frac{v^3 (v-b)^2}{2 a (v-b)^2 - R T v^3} \right)}{R T v^3 (v-b)} \\ h &= \frac{R T v^3 (v-b)}{2 a (v-b)^2 - R T v^3} \quad (117) \end{aligned}$$

**Difference of the Specific Heats.**—By equation (62')  $C - c = T \left( \frac{\delta^2 f}{\delta T \delta v} \right)^2 / \left( \frac{d^2 f}{d v^2} \right)_T$  substituting the values of the various partial differentials from Van der Waals' equation, we obtain

$$\begin{aligned} C - c &= - \frac{T R^2}{(v-b)^2} \left( \frac{v^3 (v-b)^2}{2 a (v-b)^2 - R T v^3} \right) \\ \therefore C - c &= \frac{- T R^2 v^3}{2 a (v-b)^2 - R T v^3} \quad (118) \end{aligned}$$

If the entropy, temperature, and volume are given,  $c$  can be calculated from (113), and  $C$  is then equal to:

$$c = \frac{T R^2 v^3}{2 a (v-b)^2 - R T v^3}$$

and can always be found. Another expression for  $C$  follows from its definition  $C = \left( \frac{d Q}{d T_p} \right)$ , or  $C = T \left( \frac{d S}{d T} \right)_p$

Substituting the value of  $\frac{d S}{d T}_p$ , obtained from equation (113), we find

$$C = c d T + \frac{R T \delta v}{v-b}, \text{ or } C = c d T + \frac{R T f'(p, T)}{f(p, T) - b}$$

$C$  is thus shown to depend upon both  $T$  and  $p$ , as could be readily predicted. The specific heat at constant volume, however, is different, for by the perfectly general equation (50)  $\frac{\delta c}{\delta v} = T \frac{\delta^2 p}{\delta T^2}$ ; but  $\frac{\delta p}{\delta T} = \frac{R}{v-b}$  for a Van der Waals body at constant volume,  $\therefore \frac{\delta^2 p}{\delta T^2} = 0$ , from which it follows that  $\frac{\delta c}{\delta v} = 0$ , which means that the specific heat at constant volume depends only on the temperature.

**Work Done During an Isothermal Expansion.**—In general, when the pressure is normal and uniform,  $d w = p d v$ ; substituting for  $p$  from equation (108), we have:  $d w = -\frac{a}{v^2} d v + \frac{R T d v}{v-b}$ . Integrating between  $v_1$  and  $v_2$  gives

$$w = +\left(\frac{a}{v}\right)_{v_1}^{v_2} + R T \log (v-b)_{v_1}^{v_2}$$

or

$$w = -a\left(\frac{v_2-v_1}{v_2 v_1}\right) + R T \log\left(\frac{v_2-b}{v_1-b}\right) \quad (119)$$

**Work Done During an Adiabatic Expansion.**—Here

$$w = -\int_{u_1}^{u_2} d u = J c (T_1 - T_2) - a\left(\frac{v_2-v_1}{v_2 v_1}\right) \quad (120)$$

as was found in equation (114). The term  $\frac{a(v_2-v_1)}{v_2 v_1}$  appears in both kinds of expansion (see 119 above), and evidently represents the amount of energy that disappears in the work of separating the molecules against their mutual attraction. This item would, of course, be the same in the case of a Van der Waals body ex-

panding between the same volume limits, whether that expansion were isothermal or adiabatic.

**Work Done During a Carnot Cycle.**—Since this cycle is made up of two isothermal events, and two adiabatic events, by applying equations (119) and (120) around a cycle defined by  $T_1$  and  $T_2$ , and volumes  $v_1, v_2, v_3, v_4$ , we have:

$$\text{Isothermal expansion } w_{1,2} = R T_1 \log \left( \frac{v_2 - b}{v_1 - b} \right) - a \left( \frac{v_2 - v_1}{v_2 - v_1} \right)$$

$$\text{Adiabatic expansion } w_{2,3} = c (T_1 - T_2) - a \left( \frac{v_3 - v_2}{v_3 v_2} \right)$$

$$\text{Isothermal compression } w_{3,4} = R T_2 \log \left( \frac{v_4 - b}{v_3 - b} \right) - a \left( \frac{v_4 - v_3}{v_4 v_3} \right)$$

$$\text{Adiabatic compression } w_{4,1} = c (T_2 - T_1) - a \left( \frac{v_1 - v_4}{v_1 v_4} \right)$$

Summing these up, we obtain:

$$\Sigma w = R T_1 \log \left( \frac{v_2 - b}{v_1 - b} \right) + R T_2 \log \left( \frac{v_4 - b}{v_3 - b} \right) \quad (121)$$

which is the actual work accomplished.

## CLAUSIUS' EQUATION

Unfortunately careful measurements, in an attempt to establish the validity of Van der Waals' equation, fail to justify it as completely as was hoped, and this is the case, no matter what values are taken for the constants. It appears that where this equation fails most signally is in assuming that the intermolecular attractions vary with the volume only, and are independent of the temperature. We have no reason for making such an assumption, although just how the temperature can affect such forces is far from obvious.

These considerations led Clausius to formulate an equation in which the discrepancy just mentioned was allowed for, and which results in a much closer approximation to the actual behavior of gases, than does the equation of Van der Waals. Clausius statement is:

$$\left(p + \frac{D}{T(v+B)^2}\right)(v - \epsilon) = R T . . . \quad (122)$$

This approximates to  $p(v - \epsilon) = R T$ , when  $p$  is very large at ordinary temperatures, or when  $T$  is very high. On the other hand if the pressure is very small, the specific volume becomes enormous, and the equation practically reduces to  $p v = R T$ . Ordinarily, however,

the term  $\frac{D}{T(v+B)^2}$  plays an important rôle, and denotes not only that the internal attraction between the molecules depends on a function of the specific volume, but also that it varies inversely as the temperature. This

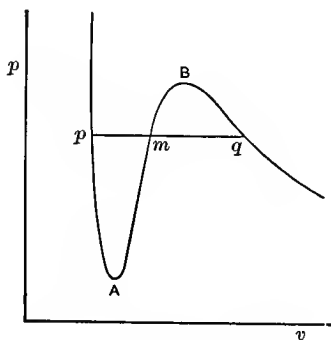


FIG. 23.

equation, like that of Van der Waals, is a cubic in  $v$ , and an analytic investigation of its properties shows that between certain values of  $p$ , there are three real roots, but outside those limits, two roots become imaginary. The plot of the equation on the  $p v$  diagram is similar to

Van der Waals' in general characteristics, and the same reasoning as to the area of the two loops is still applicable, so we may determine the points  $p$  and

$q$  by laying off a horizontal such that the areas  $p A m$  and  $m B q$  are equal. Further  $A$  and  $B$  are located as before by the condition that  $\frac{\delta p}{\delta v} = 0$ , and the point of inflection  $m$  is located by the condition  $\frac{\delta^2 p}{\delta v^2} = 0$ . Both these derivatives are readily obtained by solving (122), for  $p$ , which then becomes,

$$p = \frac{RT}{v - \epsilon} - \frac{D}{T(v+B)^2} \quad . \quad . \quad . \quad (123)$$

A combination of these two conditions determines, as before, the critical point, and we find the following critical values of  $v$ ,  $p$  and  $T$ .

$$v_c = 3\epsilon + 2B \quad . \quad . \quad . \quad (124)$$

$$T_c = \sqrt{\frac{8D}{27R(\epsilon+B)}} \quad . \quad . \quad . \quad (125)$$

$$p_c = \sqrt{\frac{1}{216} \frac{DR}{(\epsilon+B)^3}} \quad . \quad . \quad (126)$$

The law of corresponding states does not apply exactly to a body defined by Clausius' equation, because there are four constants instead of three, and by a transformation to three new variables, it is only possible to eliminate three of the constants, so the resulting equation will still depend, to a certain extent, upon the nature of the particular gas considered.

**Determination of  $l$ .**—Using the equation of Clapeyron,  $l = T \frac{\delta p}{\delta T}$  as applied to a Clausius body, we find

$$l = T \left\{ \frac{R}{v - \epsilon} + \frac{D}{T^2(v+B)^2} \right\}$$

$$\text{or } l = \frac{TR}{v - \epsilon} + \frac{D}{T(v+B)^2}$$

but since by (123)  $\frac{TR}{v-\epsilon} = p + \frac{D}{T(v+B)^2}$  we may write

$$l = p + \frac{2D}{T(v+B)^2} \quad \dots \quad (127)$$

**Determination of the Intrinsic Energy.**—By equation (4),  $dq = c dT + l dv$ , hence for “hydrostatic” pressure, we may write,

$$du = c dT + (l - p) dv$$

$$\text{or } du = c dT + \frac{2D}{T(v+B)^2} dv$$

which gives on integration

$$u_1 = u_2 + c(T_1 - T_2) + \frac{2D}{T_1} \left( \frac{v_1 - v_2}{(v_1 + B)(v_2 + B)} \right) \quad (128)$$

Here the third term is evidently due to the change in intrinsic energy caused by the change of volume (or  $\Delta u_T$ ) thus corresponding to the third term of equation (114); but, unlike (114), the temperature also appears in this term. The second term is clearly  $\Delta u_v$ , or the change of intrinsic energy at constant volume. Therefore, the whole equation might be written  $u_1 - u_2 = \Delta u = \Delta u_v + \Delta u_T$

The two preceding cases show how we can derive various functions of a Clausius body. They are not quite so readily obtained as in the previous case, and, indeed, most of them can only be expressed symbolically.

**General Equation for Real Gases.**—As has already been pointed out, the various equations for real gases take the form of,

$$(p + \pi)(v - \phi) = RT, \text{ where } \pi = f(v, T) \text{ and } \phi = f(v) \quad (i)$$

Since  $\pi$  is independent of the pressure, the equation may be solved for  $p$ , giving

$$p = \frac{RT}{v - \phi} - \pi \quad \dots \quad (ii)$$

and it is then possible to obtain an expression for the differential of intrinsic energy.

Combining equation (4) with (42) we have

$$d q = c d T + T \left( \frac{d p}{d T} \right)_v d v$$

hence  $d u = c d T + T \left( \frac{d p}{d T} \right)_v d v - p d v$ . Substituting for  $p$  and  $\frac{d p}{d T}$  their values obtained from (ii) above, we have

$$d u = c d T + \pi d v - T \left( \frac{d \pi}{d T} \right)_v d v$$

The last term is extremely small, for the influence of the temperature on intermolecular attractions is of far less importance than the influence of the volume. Hence

$$d u = c d T + \pi d v, \text{ nearly.}$$

With the aid of this equation we obtain an interesting inequality. Substituting this value for  $d u$ , in  $d q = d u + p d v$ , gives

$$d q = p d v + c d T + \pi d v \quad . \quad . \quad (iii)$$

but, in general, by (4)  $d q = l d v + c d T$ . Subtracting (iii) from (4) gives  $p d v = (l - \pi) d v$  or  $p < l$ . We have seen that  $p = l$  in the case of perfect gases, and it is interesting to note that when the intrinsic energy does not all depend on the temperature, the heat capacity  $l$  is greater than the pressure.

**Cooling of Real Gases by Expansion.**—A very important property of gases, which depends upon their intermolecular forces, and is not attributable to such imaginary bodies as perfect gases, is the cooling, which all but hydrogen experience, when they expand without doing external work.

As has already been proved, there is always a cooling produced when a body expands adiabatically in the performance of external work, but when no external work is done, it does not necessarily follow that such a cooling must take place. For instance, if we consider a perfect gas, then  $dU = dQ - dW$ , or, for unit mass,  $c dT = dq - dw$ ; if the expansion is adiabatic,  $dq = 0$ , hence  $c dT = du = -dw$ , showing that the work is done at the expense of intrinsic energy and so results in a lowering of the temperature of the gas. But if the expansion is such that no external work is done, then  $dw = 0$  and  $c dT = 0$ , which shows that  $T$  remains constant. This, of course, follows directly from the fundamental notion of perfect gases; *i.e.*, that their intrinsic energy depends only on the temperature and, therefore, if there is no change in the former, the latter must be constant.

But in the case of real gases the intrinsic energy depends, as we have seen, upon the distances between the particles that compose the gas, as well as upon the temperature, therefore during an expansion there might readily be a change in the relative proportions of these two energy components, and even in the case of an expansion where no external work is done there can occur a shift from the temperature kind to the intermolecular kind, thus lowering the temperature without altering the total quantity of energy. This is what actually occurs in the expansion of real gases when they do not perform external work. The cooling, though small in most cases at ordinary temperatures and pressures, becomes increasingly pronounced as the gas approaches its critical temperature, and as it deviates



more and more from the condition that is described by the equation  $p v = R T$ .

**Experimental Verification.**—The experimental realization of an expansion without the performance of external work is, at first sight, rather difficult. The ideal experiment would be to allow the gas to expand from a chamber of high pressure into one exhausted to a perfect vacuum; but this is clearly impossible, even if a perfect vacuum could be obtained, because, after the first



FIG. 24.

minute portion of gas had passed through, the vacuum would be destroyed, and the pressure would, of course, increase until it was the same in both chambers. Such a device, however, really does fulfil the requirement that  $d w = 0$ . For consider the arrangement indicated in Fig. 24. Let a perfect gas under pressure in *A* be allowed to expand into *B*, which has been previously exhausted. During the process of expansion work is done in the chamber *B* upon the gas collecting there, with a consequent rise of temperature. But this energy is supplied by the gas in *A*, which in consequence falls in temperature, since the process is practically adiabatic, as usually conducted. At the end of the expansion, certainly no external work has been done by the gas considered as a whole; but there has only been a slight shift of energy from one portion of the total quantity of gas to another, thus cooling the former and warming the latter. This difference of temperature will gradually

disappear, as thermal equilibrium is established, and if the final temperature of the apparatus were then the same as at first, the theory relative to perfect gases would be established; *i.e.*, that the temperature remains constant during an adiabatic expansion without the performance of work.

**Joule's Experiment.**—This experiment was actually performed by Joule in 1845. In his apparatus the two vessels were immersed in water contained in a double-walled tank so that any change in temperature of the gas would result in warming or cooling the water. But, after equilibrium had been established both in the gas and surrounding water, no such change was observed, even with a very delicate thermometer. He then repeated the experiment, having each vessel in a separate water bath, and in this way he was able to detect the temporary heating of one portion of the gas, and corresponding cooling of the other; but, as these appeared to be equal, he concluded that no change of temperature of the total mass resulted, and that air behaved like an ideal gas. In the light of later observations it is easy to account for Joule's failure to detect the cooling of a gas during unresisted expansion. With a comparatively small expansion ratio, the actual cooling would be small, and when we consider the minute heat capacity of the gas compared to that of the surrounding water, it is not surprising that the temperature of the latter was not appreciably lowered, in supplying heat to make up the slight deficit in the gas.

**Porous Plug Experiment.**—In 1852 Lord Kelvin (then Sir William Thomson) and Joule tested this principle by another and much more delicate method,

and succeeded in detecting a change in temperature during unresisted expansion, due to a change in the distribution of the intrinsic energies of the gas. The experiment is a very celebrated one and is known as the Joule-Thomson porous plug experiment. It consists in forcing a gas slowly through a plug of some porous material into a receiver where the pressure is constant. Thermometers are placed on either side of the plug, and also at some distance from the plug on the low-pressure side to indicate the final temperature. In spite of the slowness with which a gas passes through such an obstacle, there will be eddies set up in it, which involve an increased kinetic energy. This means (if the process is strictly adiabatic) that there must be a fall in temperature, to supply the mechanical energy represented by the eddies, at the expense of the thermal energy of the gas itself. Such an effect would appear in an ideal gas just as much as in a real one, and has nothing to do with the phenomenon the experiment was designed to detect. At a point sufficiently far removed from the plug, however, we may consider that the eddies have subsided, and if the thermometer placed at a distance from the plug records a temperature different from that of the compressed gas, it would seem to be due to an effect which does not appear in perfect gases.

It was assumed in the experiment that the whole process was adiabatic; that is, performed in vessels whose walls were strictly non-conducting. In such a case the total energy of the gas remains constant. It was further assumed that the heat lost on account of the eddies would be given back to it when the eddies had subsided a short distance from the plug, therefore the

only uncompensated change of temperature was the one sought. It should be remarked, however, that there is always a slight warming of the plug itself due to friction. This irreversible flow of energy will cause a corresponding cooling of the gas, unless the heat thus produced is restored to it by the slow process of conduction; but this error is extremely small if the flow is sufficiently slow, and may be neglected.

Another experimental method consists in enclosing the low-pressure receiver in a calorimeter in such a way that the quantity of heat which must be supplied to maintain the temperature constant, after a known mass of gas has passed through the plug, can be accurately measured.

Joule and Thomson examined a number of gases, and found a distinct cooling in all cases, except that of hydrogen. This gas behaves anomalously in its deviation from Boyle's law, and its heating during unresisted expansion has not been fully explained.

**Temperature of Inversion.**—The anomalous heating of hydrogen at ordinary temperatures, it should be remarked, is less and less pronounced as the temperature is lowered; at  $-80^{\circ}$  C. it changes sign, and below this temperature behaves like other gases. On the other hand, with rising temperature, the other gases show a less and less pronounced cooling effect, and a reversal would probably take place so that they would heat during expansion, if the experiment could be performed at a sufficiently high temperature. Thus each gas has a *temperature of inversion*, as it is called, and apparently hydrogen only differs from the others in that its temperature of inversion is lower than that at which the

experiment is usually performed, while those of the other gases are much higher.

**Correction of the Constant Pressure Gas Thermometer.**—The porous plug experiment is of the highest importance in its application to the determination of the corrections to be applied to the gas thermometer, in order that it may be used to read temperatures referred to any arbitrary zero, but in absolute degrees; and also in the determination of the temperature of melting ice in absolute degrees above the absolute zero.

It has already been shown that a perfect gas, expanding without doing external work, will remain at constant temperature and therefore  $p_1 v_1 = p_2 v_2$ . But when a real gas expands in this way, we can no longer write  $p_1 v_1 = p_2 v_2$ ; for although no external work has been done, there has been internal work in separating the molecules against their mutual attractions. This results in lowering the temperature; or a certain amount of kinetic energy has been given up by the gas, to become potential energy in the increased separation of the molecules. This loss of kinetic energy can be measured, according to the kinetic theory of gases, by the difference between the energy per unit mass before expansion, and after; that is  $p_1 v_1 - p_2 v_2$ , which in general does not equal zero, and is usually positive. This is because  $p v$  is the work that would be required to force the unit mass into the receiver against the pressure  $p$ . Hence the work done during expansion, which is transformed into potential energy of the molecules, is  $\int_1^2 d w = p_1 v_1 - p_2 v_2$ , or  $d w = d (p v)$

The first law of thermodynamics,  $d q = d u + d w$ , now

takes the particular form for this case of unresisted expansion

$$d q = d u + d (p v), \quad . \quad . \quad (129)$$

where  $d q$  is an exact differential, being the sum of two exact differentials, and is identical with the thermodynamic potential  $d f_{Sp}$ . But, whatever the process, we can always write  $d u = d q - p d v$  for the change of intrinsic energy, since it depends only on the initial and final states; combining this with equation (3), we obtain  $d u = C d T + h d p - p d v$ . Substituting for  $d u$  in (129) there results,

$$\begin{aligned} d q = d f_{Sp} &= C d T + h d p - p d v + d (p v) \text{ or} \\ d f_{Sp} &= C d T + (h + v) d p \quad . \quad (130) \end{aligned}$$

which must be equal to zero if the gas neither receives nor loses heat. Or, what is the same thing,  $f_{Sp}$  is constant in the porous plug experiment. By equation (45)

$h = -T \left( \frac{d v}{d T} \right)_p$ , therefore (130) becomes  $C d T - T \left( \frac{d v}{d T} \right)_p d p + v d p = 0$ . Dividing by  $d p$ , and writing  $\frac{d T}{T} = d \log T$ , we have

$$(d \log T)_p = \frac{(d v)_p}{v + C \frac{d T}{d p}} \quad . \quad . \quad (131)$$

which is the correction equation for the constant pressure gas thermometer.

The determination of the quantity  $C \frac{d T}{d p}$  may be made in two ways, either by observing the fall of temperature during a strictly adiabatic expansion, or by

measuring the quantity of heat that must be supplied from a surrounding calorimeter to keep  $T$  constant. These methods are practically identical in result, for a small variation of the pressure; but the latter is to be recommended, as it is not subject to the errors that may arise in measuring the change of temperature directly, on account of the irreversible cooling, due to eddies, that has already been mentioned.

Assuming that the latter method is adopted, we can calculate, from the quantity of heat supplied, the change of temperature that would result if the heat had not been added, and so obtain a series of values for  $\frac{dT}{dp}$  for a small variation of  $p$ , and at various specific volumes; and then determine the variation of  $\frac{dT}{dp}$  as a function of  $v$ . This quantity is nearly constant within certain limits of the volume; and, in any case,  $C\frac{dT}{dp}$  which is a measure of the "cooling effect" is small compared to  $v$ , so that an average value may be used (as was done by Kelvin) with sufficient precision.

The derivative  $\frac{dT}{dp}$  should be expressed in terms of degrees on the scale of the gas thermometer that is under examination, and  $C$  must also be measured in terms of the same scale, and a value chosen that corresponds to the range of  $v$  and  $T$  that is actually used. Then taking the experimentally found value of  $C\frac{dT}{dp}$ , or the "cooling effect," which is regarded as constant over the range to be considered, we can integrate the equation between the chosen limits of temperature and

volume, thus obtaining an expression for the ratio of temperatures on the absolute scale, corresponding to a given volume ratio as measured by the gas thermometer.

Setting  $C \frac{dT}{dp} = X$ , and integrating between  $T_1$  and  $T_2$ , the equation (131) becomes

$$\left[ \log \frac{T_1}{T_2} = \log \frac{v_1 + X}{v_2 + X} \right]_p \quad . \quad . \quad . \quad (132)$$

If there is no cooling effect (*i.e.*, if the gas is perfect) then  $X = 0$ , and the above equation reduces to the familiar  $\left[ \frac{T_1}{T_2} = \frac{v_1}{v_2} \right]_p$ .

Equation (132) may be transformed to

$$\left[ \frac{T}{T_2 - T_1} = \frac{v_1 + X}{v_2 - v_1} \right]_p$$

In this form it is applicable to the determination of the absolute temperature of the freezing of water; for, let  $T_1$  be that temperature, and let  $T_2$  be the temperature of boiling water, while  $v_1$  and  $v_2$  are the corresponding volumes as measured in the thermometer; since  $T_2 - T_1 = 100$  on the absolute scale, it is evident that  $T_1$  is determined.

#### Correction of Constant Volume Gas Thermometer.—

If the porous plug experiment is used as a basis for standardizing this thermometer, we start as in the previous case with the condition that  $f_{Sp}$  is constant, or  $df_{Sp} = du + d(pv) = 0$ , but by equation (4)  $dq = c dt + l dv$ , and since  $du = dq - p dv$ , we obtain,  $df_{Sp} = c dT + l dv - p dv + d(pv) = 0$ . Expanding  $d(pv)$ , this becomes  $c dT + l dv + v dp = 0$ .



Substituting  $l = T \left( \frac{dp}{dT} \right)_v$  and dividing by  $dv$  gives

$$c \frac{dT}{dv} + T \left( \frac{dp}{dT} \right)_v + v \frac{dp}{dv} = 0, \text{ or } c \frac{dT}{dv} + \left( \frac{dp}{d \log T} \right)_v + v \frac{dp}{dv} = 0, \text{ hence}$$

$$(d \log T)_v = \frac{dp_v}{-v \frac{dp}{dv} - c \frac{dT}{dv}} \quad . \quad . \quad (133)$$

This equation is very similar to (131), with  $p$  in place of  $v$ , but there is one important difference, where  $-v \frac{dp}{dv}$  appears instead of  $+p$ , as we should expect. This term, indeed, is equal to  $+p$ , for a perfect gas at constant  $T$ ; but its actual determination for a real gas is difficult, and makes the correction of the constant volume thermometer in this way inadvisable.

A better way to obtain the correction of the constant volume thermometer would be to use the original experiment of Joule, in which the gas is allowed to rush into a vacuum. In this case, if the process is adiabatic,  $dw$  and  $dq$  are both zero, therefore  $du = 0$ , also, and the fundamental condition is  $du = dq - p dv = 0$ , instead of  $df_{sp} = 0$ , as in the porous plug experiment. Substituting for  $dq$  from equation (4), we have  $du = c dT + (l - p) dv = 0$ . But  $l = T \left( \frac{dp}{dT} \right)_v$ , hence  $c dT + T \left( \frac{dp}{dT} \right)_v dv - p dv = 0$ . Setting, as before,  $\frac{dT}{T} = d \log T$ , dividing by  $dv$ , and transposing, this reduces to

$$(d \log T)_v = \frac{\left( \frac{dp}{dT} \right)_v}{p - c \frac{dT}{dv}} \quad . \quad . \quad (134)$$

In this equation  $c \frac{dT}{dv}$  is to be found by direct observation of the cooling resulting from the expansion. Both  $c$  and  $T$  must be known in terms of the gas thermometer scale; and, since the value of  $c$  depends upon  $T$ , it should be accurately determined within the region of the temperatures to be measured. As in the case of the porous plug experiment, the cooling could be determined indirectly by measuring the quantity of heat required to maintain the gas at constant temperature, which would offer fewer experimental difficulties than the direct observation.

Although Joule's method is open to serious objections, as has been pointed out, in this case it is preferable to the porous plug, because we have only to observe the cooling effect, and are not obliged also to determine  $d p/d v$  for the gas, which would be necessary if the latter method were used to standardize the constant volume thermometer.

**Cooling of a Clausius Body.**—The lowering of the temperature of a gas in the porous plug experiment may be predicted by assuming the gas to follow some characteristic equation, such as that of Clausius. Starting with our fundamental condition,  $df_{Sp} = du + d(pv) = 0$ , we may integrate between limits giving  $u_1 - u_2 + p_1 v_1 - p_2 v_2 = 0$ ; substituting for  $u_1 - u_2$ , from equation (128), this becomes,

$$c(T_1 - T_2) + 2 \frac{D}{T_1} \frac{v_1 - v_2}{(v_1 + B)(v_2 + B)} + p_1 v_1 - p_2 v_2 = 0 \quad (i)$$

If  $v$  is large, we may neglect  $B$  in comparison, and may eliminate  $v_1$  and  $v_2$  by  $p v = R T$ , which was shown to

be justifiable (p. 116), when the density is small. The second term, or  $\Delta u_T$ , then reduces to

$$\Delta u_T = \frac{-2 D(p_1 - p_2)}{R T_1^2} \cdot \cdot \cdot \cdot \quad (ii)$$

therefore (i) becomes

$$c(T_2 - T_1) = -\frac{2 D(p_1 - p_2)}{R T_1^2} + (p_1 v_1 - p_2 v_2) \quad (iii)$$

which gives the cooling desired. But equation (iii) may be expressed in a form more convenient for comparison with the experimental cooling, if we eliminate the volume altogether. This is done with the aid of Clausius' equation, yielding approximately,\*

$$c(T_1 - T_2) = \left( \frac{3D}{R T_1^2} - \epsilon \right) (p_1 - p_2) \cdot \quad (135)$$

in which  $T_1 - T_2$  gives the fall of temperature desired, in terms of known constants and the initial temperature  $T_1$ .

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\* See Bouasse, "Cours de Physique," tome 2, p. 39.

## CHAPTER VII

### CHANGE OF STATE

IN applying the principles of pure thermodynamics we have hitherto considered only bodies whose condition was a continuous function of the temperature, pressure, and volume; and, though there were certain critical points in the curve representing the function, we dealt with them as if they underwent no radical changes with changing conditions. This is strictly true for gases above the critical temperature, and below that temperature, if we adopt an equation like Van der Waals', there is no point of discontinuity that would lead us to predict any abrupt transformation resulting from a continued change in one of the independent variables.

In this chapter, however, we shall study particularly the conditions involved when a body, without chemical alteration, undergoes a transformation in structure as from vapor to liquid, or liquid to solid, or the reverse; and we shall also see that, as we become more specific in prescribing the state of a body, fewer quantities, like those we have discussed, are needed to determine its precise condition. That is, the number of independent variables that describe it is diminished.

**Definitions.**—But before proceeding to discuss any particular case, we must explain certain terms that will be used, and derive an important generalization, known as the *phase rule*, which is applicable to any

single body or mixture of bodies having any number of independent variables, and existing in any number of states.

A *Complex* is a mixture of substances in chemical equilibrium, in which the quantity of any one may be varied continuously without altering the chemical constitution of the whole.

A *Component* is one of the independent bodies that go to form a complex; the components comprise the smallest number of *independently variable* constituents needed by this complex. Thus if we have a mixture of  $\text{PCl}_5 + \text{Cl}_2 + \text{PCl}_3$ , there are only two components, for any two of the substances named can be regarded as those two, but the third is not independent as is readily seen from the chemical equilibrium  $\text{PCl}_3 + \text{Cl}_2 \rightleftharpoons \text{PCl}_5$ . Moreover, a component must be capable of *continuous variation*; hence water cannot be regarded as a complex containing the components H and O, except near the temperature of dissociation when a complex arises, that is described by  $\text{H}_2 + \text{O} \rightleftharpoons \text{H}_2\text{O}$ .

A *Phase* is a condition of equilibrium of a given homogeneous component that resists fractioning. Thus water is a phase, ice and steam are phases of the single component, water. A solution such as salt and water represents a phase also, but in this case a phase having two components instead of one.

*Degree of Freedom* or *Variability* of a system or complex is the number of independent variables that are needed to define it.

**Chemical Potential.**—This quantity, which will be designated by  $\mu$ , is a measure of affinity for hydrogen. If the two bodies, *A* and *B*, are separated by a membrane

permeable to hydrogen only, as platinum, for instance, then if  $H$  moves from  $B$  toward  $A$ , the latter is said to have the higher potential. This quantity,  $\mu$ , includes the notion of physical potential as well, so that if some physical cause, such as temperature, should make the hydrogen move toward  $B$  instead,  $B$  would then be at a higher potential.

**The Phase Rule of Gibbs.**—Let us imagine a mixture of  $n$  components existing in  $\phi$  different phases. If we consider the total intrinsic energy of a single one of these phases, we shall have the sum of the ordinary intrinsic energy  $T dS - p dV$ , of that phase, plus all the chemical energies represented by the potentials  $\mu_1 \dots \mu_n$ , of the  $n$  components. Suppose the masses of these components present be  $m_1, m_2 \dots m_n$ , then

$$dU = T dS - p dV + \mu_1 d m_1 + \mu_2 d m_2 + \dots \mu_n d m_n \quad (i)$$

Integrating between 0 and any finite value we obtain

$$U = TS - pV + \mu_1 m_1 + \mu_2 m_2 + \dots \mu_n m_n \quad (ii)$$

From this equation we might determine any of the chemical potentials by the obvious relation

$$\mu_1 = \left( \frac{dU}{d m_1} \right)_{S, V, m_2, \dots, m_n}$$

Taking the complete differential of (ii), we have  $dU = T dS + S dT - p dV - V dp + \mu_1 d m_1 + m_1 d \mu_1 + \dots$  from which (i) may be subtracted, giving a fundamental equation which completely defines the state of a single phase made up of  $n$  constituents; or

$$S dT - V dp + m_1 d \mu_1 + m_2 d \mu_2 \dots m_n d \mu_n = 0 \quad (136)$$

Now it is evident that if there are  $\phi$  phases present in the complex, there will be  $\phi$  such equations. In each

equation there are  $n + 2$  variables, namely  $p, T$  and  $\mu_1, \dots, \mu_n$ , therefore the number of degrees of freedom of such a system is the number of variables less the number of equations, or phases, hence,

$$(n + 2) - \phi = v, \quad \dots \quad (137)$$

or the “variance” of the system. This equation is Gibbs’ celebrated phase rule and is of great value in the study of mixtures of substances and phases in equilibrium with each other. Evidently each new phase diminishes the “variance” by one, and each new component raises it by one. Now it will be remembered that 2 is the number of *independent* physical quantities that enter into the determination of the state of a system, according to our fundamental postulate. In case more enter in, as for instance the electrical potential of the body, we should have to write  $n + 3$ , in place of  $n + 2$  in equation (137), hence a more general expression would be  $(n + n') - \phi = v$ , where  $n$  is the number of chemically independent variables, and  $n'$  is the number of physically independent variables.

**Various Classifications.**—A complex may be classified according to its *order*, as determined by the value of  $n$ , or according to its *degree*, as determined by  $\phi$ . Suppose we consider a complex of one component. There are three possible cases

$$(1 + 2) - 3 = 0, \text{ an invariant system,}$$

$$(1 + 2) - 2 = 1, \text{ a univariant system,}$$

$$(1 + 2) - 1 = 2, \text{ a bivariant system.}$$

It is evident that there cannot be more than three phases, because this would mean a negative variance, which is absurd.

Water at the triple point is a good illustration of the first case, for then there is one component existing simultaneously in the three phases: ice, water, and steam. Water and saturated steam in equilibrium illustrate the second case, and dry superheated steam, or a gas, represents the third case.

Now let  $n = 2$ . Four cases are now possible:

$$(2 + 2) - 4 = 0$$

$$(2 + 2) - 3 = 1$$

$$(2 + 2) - 2 = 2$$

$$(2 + 2) - 1 = 3$$

The first case is exhibited by two kinds of crystals of the same chemical constitution in equilibrium with the liquid and vapor of the same substance. The second case is shown by an ordinary solution in which part of the dissolved body exists in crystalline form, and part of the liquid is vaporized. The third case is shown by a solid and liquid of different chemical nature in equilibrium, or a solid and a vapor, or a liquid and a vapor. The fourth is the case of a mixture of two solids (as an alloy), a mixture of two liquids, or of two vapors or gases. This last case cannot be described by a system of curves on a plane surface, as on a  $p$   $T$  diagram, for instance, but a third axis must be introduced to represent the third degree of freedom. This third axis is usually taken as the concentration, and the various states of the complex are then represented by a solid in  $p$ ,  $T$  and  $C$ , where  $C$  is the concentration. This solid is bounded by surfaces which are bivariant regions, and the surfaces intersect in univariant lines, and, if these edges meet, their intersection is an invariant point.



**Complexes of One Component.**—We shall, for the present, limit ourselves to complexes having but one component, and there will be no need of the third axis, in graphic representations of their behavior; but plane curves having various coördinates will be used. The temperature-pressure diagram of water in the neigh-

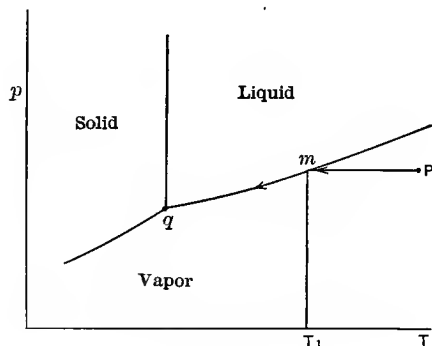


FIG. 25.

borhood of the triple point is familiar, and serves as an excellent application of the phase rule. In general any point  $P$  (Fig. 25) on this plane represents the state of a bivariant system; however, if we move along a line of equal pressure as indicated, we shall at some temperature,  $T_1$ , intersect one of the lines that mark univariant regions, such as the saturated steam line between the liquid and vapor regions. In the case assumed, a new phase is gained at the point  $m$ , or water, and one degree of freedom is lost. Now, moving along the steam line we ultimately arrive at  $q$  where three lines meet. At this point (and there is only one such for water) a second phase (ice) is gained and the one remaining

degree of freedom is lost. This, the triple point, then represents the state of an invariant system.

**Univariant Systems.**—These systems are of such continual occurrence in nature, and applied science, that we shall now discuss them at considerable length. Referring to Fig. 26 which, as has already been explained,

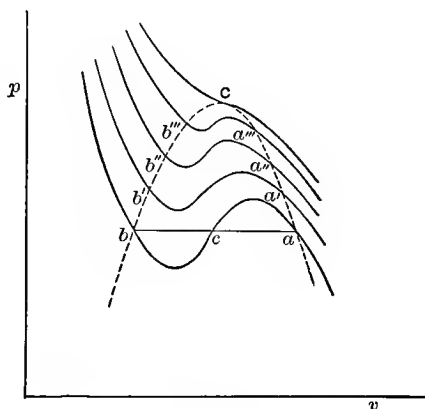


FIG. 26.

represents a system of isothermals of a Van der Waals body on the  $p v$  diagram, we note that the locus of the points  $a$  and  $b$  is a curve having a single maximum, at the critical point,  $C$ . This curve,  $a C b$ , encloses an area which is a univariant region, as far as the variables  $p$ ,  $v$  and  $T$  are concerned. The points  $a$ ,  $a'$ ,  $a''$  . . . are the locus of a dry saturated vapor; the points  $b$ ,  $b'$ ,  $b''$  . . . are the locus of a liquid at the temperature of vaporization; while the space between is a mixture of both phases at the boiling point. Outside the curve,  $a C b$ , is a bivariant region, but points on

the curve itself are univariant, and denote the limiting case where one of the phases is just making its appearance. This bounding region has peculiar properties which will be discussed later.

**Latent Heat.**—The change in molecular arrangement involved in passing from  $b$  to  $a$  (or a similar process when we pass from the solid to the liquid condition) requires either an addition or subtraction of heat according to whether the change is toward greater or less molecular freedom. This transformation is reversible, and is accompanied by changes in internal structure which do not alter the body's temperature. It is therefore permissible to apply the second law of thermodynamics in the form  $\frac{1}{T} \int_b^a dq = \int_b^a ds$ , since  $T$  is constant. But  $\int dq$  is the quantity of heat used in producing an isothermal transformation, and is, therefore, the familiar latent heat  $L$ . Integrating then, we find

$$L = T (s_a - s_b) . . . . (138)$$

The latent heat is positive if  $s_a > s_b$ , which indicates an absorption of heat when we move from a point of lower to one of higher entropy. In most isothermal transformations, at constant pressure, this means an increase in volume, or motion toward the right on the  $PV$  diagram, but in the case of melting ice, the change is toward the left.

Another expression for the latent heat was obtained in equation (43), which is a form of the equation of Clapeyron. But it was shown by Gibbs that this equation may be obtained directly from the system of

equations (136), from which he derived his phase rule. In the univariant systems we are considering, two phases exist simultaneously in equilibrium, and (136) is thus applicable to both; moreover, when there is but one component  $n = 1$ , and we obtain

$S_a dT - V_a dp + m_a d\mu = 0$  for one phase,  
and

$S_b dT - V_b dp + m_b d\mu = 0$  for the other.

Eliminating  $d\mu$ ,

$$(m_b S_a - m_a S_b) dT = (m_b V_a - m_a V_b) dp$$

But the total entropy,  $S = ms$ , and similarly,  $V = mv$ ; making these substitutions in both phases we obtain

$s_a - s_b = (v_a - v_b) \frac{dp}{dT}$ , which combined with (138) gives

$$L = T(v_a - v_b) \frac{dp}{dT}$$

Thus the heat involved in molecular rearrangement is shown, as before, to be dependent upon the change in volume, which occurs during the change of state. At the critical temperature there is no such change,  $v_a = v_b$ , and, since  $\frac{dp}{dT}$  cannot vanish, it is clear that  $L = 0$  at that point. For temperatures higher than the critical there is no change of state and no "latent heat."

**Equilibrium of Phase.**—If we represent the transformation on the  $pT$ , instead of the  $pv$  diagram, change of state consists in crossing a boundary curve from the region "a" into the region "b," or vice versa, and points on the curve indicate the univariant region where both phases can exist simultaneously. To be specific, suppose this region "b" is the solid phase, and "a" the liquid

phase of the same substance. This does not mean that the solid phase cannot exist at all in the region "a," or liquid in the region "b," but if it does exist there, it is unstable and tends to change over to the other phase. An apparent exception is presented in such cases as that of water below  $0^{\circ}$  in the liquid state. If no ice crystals are introduced, and if it is kept perfectly quiet, it may

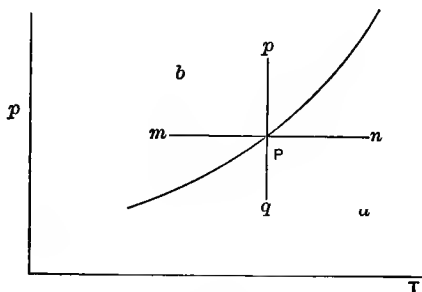


FIG. 27.

exist in a kind of stability indefinitely. This state is known as a metastable condition, or one of unstable equilibrium.

**Potential and Equilibrium.**—These ideas of equilibrium may be better expressed in terms of the thermodynamic potential  $F_{Tp}$  or  $F'$ , since we are now taking  $p$  and  $T$  as the independent variables. At the point  $P$  (Fig. 27), both phases can exist together in equilibrium, hence  $F'_b = F'_a$ . If  $x$  represents the fraction of the unit mass that is in the "a" condition, then  $1 - x$  represents the fraction that is in the "b" condition. Let  $v_a$  and  $v_b$  be the specific volumes of each phase and  $V$  the total volume of the mixture at the point  $P$ . Then the total potential of the mixture is

$$F' = F'_b(1-x) + F'_a x, \text{ or } dF' = (F'_a - F'_b) dx$$

Now any spontaneous transformation must involve a decrease in the value of  $F'$  or  $dF' < 0$  is the condition of a spontaneous change. Therefore if  $dx$  is positive,  $F'_a < F'_b$ , which means that a spontaneous increase in the ratio of phase  $a$  to phase  $b$  can only occur in the region where  $F'_b > F'_a$ . This, then, must be the region in which "a" alone is in stable equilibrium. On the other hand, if  $dx$  is negative,  $F'_a > F'_b$ , which is the condition of stability within the "b" region, where any spontaneous change means a decrease in the "a" phase. On the boundary line where both phases are in equilibrium,  $F'_a = F'_b$ , and  $dF' = 0$ , or there is no spontaneous change in either direction.

Suppose, now, that a transformation is effected at constant pressure from the point  $m$  to  $n$ , involving a change of state at  $P$ , in which  $m$  and  $n$  are supposed infinitely close to  $P$ . Then  $Pm = Pn = dT$ , hence the potential at  $m$  is

$$F'_b + \left( \frac{dF'_b}{dT} \right)_p dT$$

and at  $n$  is

$$F'_a + \left( \frac{dF'_a}{dT} \right)_p dT$$

But at  $m$ ,  $dx$  is negative, and

$$F'_a + \left( \frac{dF'_a}{dT} \right)_p dT > F'_b + \left( \frac{dF'_b}{dT} \right)_p dT$$

and since  $m$  and  $n$  are supposed infinitely close,  $F'_a = F'_b$  so the inequality becomes

$$\left( \frac{dF'_a}{dT} \right)_p dT > \left( \frac{dF'_b}{dT} \right)_p dT$$

But by equation (59) these partial derivatives are each equal to minus the entropy in their respective regions, therefore  $(S_b - S_a) dT > 0$ , or  $L > 0$  if  $dT$  is positive. Hence a transformation from  $b$  to  $a$ , which involves a tendency to raise  $T$ , means, as is obvious, a positive latent heat, and conversely a transformation that tends to lower  $T$ , means a negative latent heat.

**Change in Volume.**—The change of specific volume in passing from one state to another can be studied in the same manner. Suppose the transformation takes place along the isothermal  $p q$ , then at  $p$  we have a potential equal to

$$F'_b + \left( \frac{dF'_b}{dp} \right)_T dp$$

and at  $q$  a potential equal to

$$F'_a + \left( \frac{dF'_a}{dp} \right)_T dp$$

but if  $p$  and  $q$  are infinitely close together, we have as before, in the "a" region,

$$\left( \frac{dF'_b}{dp} \right)_T dp > \left( \frac{dF'_a}{dp} \right)_T dp$$

but by equation (59),

$$\left( \frac{dF'}{dp} \right)_T = V$$

hence  $(v_b - v_a) dp > 0$ . Therefore if  $dp$  is positive,  $v_b > v_a$ , which means that if we start in the "b" region, and an isothermal transformation to the "a" region involves a tendency to increase the pressure, then the specific volume decreases. In the case illustrated by

Fig. 27,  $d p$  is obviously negative, hence the volume increases in passing from  $p$  to  $q$ .

But the pressure-volume relations are better represented by the  $p v$  diagram. In Fig. 28 it is clear that

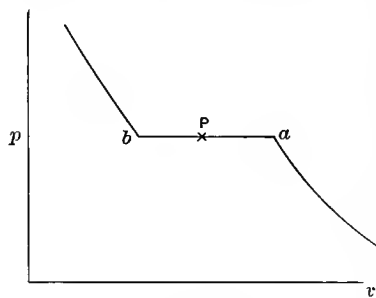


FIG. 28.

a change from the "b" to the "a" state involves an increase of volume, coupled with a tendency for  $p$  to diminish; but if  $b$  and  $a$  were to change places in the diagram,  $d p$  would be positive, and the volume would diminish. If  $a$  is supposed to possess the

higher potential, as has been assumed, then the case where  $d p$  is negative is much the more common, as it applies to all cases of vaporization, and most cases of fusion. Water is, of course, an important exception, for in passing from ice to water,  $d p$  is positive, and  $v_a < v_b$ .

**Change of  $S$  and  $U$ .**—We have so far examined the change of heat, or  $L$ , that accompanies a change of state, and the change in specific volume. There still remain to be considered the change in entropy and the change in intrinsic energy. We have already seen that  $L = T (s_a - s_b)$ , hence  $(s_a - s_b) = L/T$ , so that the entropy increases in going from  $b$  to  $a$ , if  $L$  is positive for the same transformation. Hence, in general, fusion and vaporization involve an increase of entropy which is readily computed, since  $T$  remains constant during the process. Finally, to obtain the change in  $U$ , we take  $d u = T d s - p d v$  and integrate between the



limits  $a$  and  $b$ . At constant pressure  $u_a - u_b = T(s_a - s_b) - p \int_b^a d v$ , or

$$u_a - u_b = L - p (v_a - v_b). \quad . \quad . \quad (139)$$

This equation furnishes an interesting means for the discussion of  $L$ , for  $L = \{u_a - u_b\} + \{p [v_a - v_b]\}$ . The latent heat is thus shown to consist of two parts, which signify that as we pass from one phase to another at constant temperature and pressure, the heat required to effect the transformation is partly converted into a change in the intrinsic energy of the system due to the rearrangement of the molecules, and partly into purely mechanical work against the uniform pressure to which the body is subjected. If this pressure is zero, the second item disappears, and there remains only the heat of the change of potential, which in this case is due only to the molecular rearrangement.

When  $L$  is positive the change in intrinsic energy is always positive. This is not self-evident, because from equation (139) it would seem as if  $v_a$  might be so much larger than  $v_b$  as to make  $u_a - u_b < 0$ . That this is never the case can be proved as follows: As was shown on p. 118, a combination of equations (4) and (27) gives  $du = c dT + (l - p) dv$ . Therefore at constant temperature,  $du = l dv - p dv$  or integrating

$$[u_a - u_b = (l - p) (v_a - v_b)]_T \quad . \quad . \quad (140)$$

But we have proved (p. 119) that in general  $l > p$  except in the case of perfect gases where  $l = p$ . Moreover, if  $L$  is positive,  $l$  is also, as is evident from equations (42) and (43). Therefore, if  $L$  is positive,  $l - p \geq 0$ , and  $u_a - u_b \geq 0$ , because  $v_a > v_b$  by hypothesis. In point

of fact,  $p(v_a - v_b)$  is usually very much smaller than  $L$ . At the temperature of melting water it is about  $1/19$  of  $L$  for vaporization, and in the case of boiling water at atmospheric pressure, about  $1/13$  of  $L$ .

Since by equation (43)  $L = l(v_a - v_b)$ , and since that portion of  $L$  which is concerned in overcoming the external pressure  $L' = p(v_a - v_b)$ , we obtain

$$\left[ \frac{L'}{L} = \frac{p}{l} \right]_T \quad . \quad . \quad . \quad . \quad (141)$$

At the critical temperature there is no abrupt change in the volume at constant temperature and pressure, as there is at lower temperatures, and  $v_a = v_b$  as we pass through the critical point. It follows that  $u_a - u_b = 0$  at that temperature, or there is no abrupt change in the intrinsic energy. This would be expected, as there is no change of state at the critical point, and at constant temperature  $U$  can only be increased by a change in the molecular arrangement.

Since  $v_a = v_b$  and  $u_a = u_b$ , it is clear from equation (139) that  $L = 0$  at the critical point. This has been verified experimentally for  $\text{CO}_2$ , and it is observed that in all cases  $L$  diminishes as the temperature increases, and doubtless vanishes at the critical temperature of each substance.

## VAPORIZATION

What has been said so far concerning change of state has been, in the main, of a general nature applicable to any substance and any isothermal transformation. We shall now examine in more detail the particular transformation known as vaporization, and with especial reference to water.

**Formulæ for Latent Heat of Vaporization.**—The quantity of heat absorbed in vaporizing a gramme of any substance, as has been seen, depends on the temperature, and to a much smaller degree on the pressure. Various empirical formulæ have been offered that give  $L$  approximately as a function of  $T$  and for a considerable range of temperature. For instance, Regnault proposed a formula that gives the total quantity of heat required to raise a gramme of water from  $0^{\circ}$  C. to any temperature, and then convert it completely into steam at that temperature. This equation is

$$H = 606.5 + .305 t \quad . \quad . \quad (142)$$

From this  $L$  is readily determined, since the amount of heat involved in raising one gramme of water  $t$  degrees is approximately  $t$ , hence  $L = 606.5 + .305 t - t$ , or

$$L = 606.5 - .695 t \quad . \quad . \quad (143)$$

But such formulæ are only good in very rough calculations, and are of little value near the critical point, especially if they ignore the influence of pressure as does that of Regnault. To show its inexactness, let  $L = 0$ , which is the case at the critical point; then solving for  $t$ , we find  $t = 872^{\circ}$  C., whereas the critical temperature of water is about  $365^{\circ}$  C. A more accurate method for calculating  $L$ , if the necessary data are available, is by the formula of Clapeyron in the form of equation (43); here the influence of the pressure is taken account of, but it is necessary to know  $d p / d T$  at the temperature considered, as well as the initial and final volumes. If these quantities are known  $L$  may be found with high precision, at temperatures not too near the critical.

**Liquid-Vapor Mixtures.**—Let us now examine changes

that may occur within the univariant region, where both liquid and vapor can exist together in equilibrium. Let  $AB$ , in Fig. 29, be a typical isothermal on the  $p v$  diagram. The dotted curve, as usual, is the locus of the points of discontinuity  $a$  and  $b$ . Any point as  $P$ , or  $P'$ , inside this region indicates the pressure and volume of liquid and saturated vapor in equilibrium. Now let  $x$  be the mass of vapor per gramme of the mixture, then

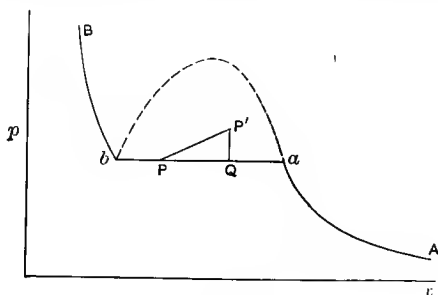


FIG. 29.

$1 - x$  = the mass of liquid per gramme of the mixture. Further let  $c$  = the specific heat of the liquid and  $c'$  = the specific heat of the vapor. (Note: when dealing with saturated vapors, we have but one specific heat, because saturated vapor is univariant and both pressure and volume are fixed by the temperature.)

The amount of heat required to vaporize an infinitesimal amount of the water is  $L dx$ . Then any transformation, as from  $P$  to  $P'$  inside the dotted curve, may be carried out in two steps; first by passing along the isothermal from  $P$  to  $Q$ , and then along a line of constant volume from  $Q$  to  $P'$ , therefore the total heat needed for the transformation is given by the sum of  $L dx$ ,

which is the heat absorbed at constant temperature, and that at constant volume, or  $[c(1-x) + c'x] dT$ , hence

$$dq = L dx + [c(1-x) + c'x] dT. \quad (144)$$

Further, let  $v'$  be specific volume of the liquid and  $v''$  be specific volume of the vapor, then  $(1-x)v' =$  the volume of the liquid present in the unit mass of the mixture, and  $xv'' =$  the volume of vapor per gramme of the mixture; hence the specific volume of the mixture at  $P$  is given by  $v = xv'' + (1-x)v'$ , or  $v = x(v'' - v') + v'$ , hence

$$x = \frac{v-v'}{v''-v'} \quad . \quad . \quad . \quad . \quad (145)$$

But  $v'$  and  $v''$  are constants at constant temperature, therefore  $dx = \frac{dv}{v''-v'}$ . Substituting these values for  $x$  and  $dx$  in (144), we obtain

$$dq = \frac{L dv}{v''-v'} + \left( c \frac{v''-v}{v''-v'} + c' \frac{v''-v'}{v-v'} \right) dT \quad (146)$$

But  $\frac{L}{v''-v'} = l$  (by equation 43), hence

$$dq = l dv + a dT \quad . \quad . \quad . \quad (147)$$

where  $a$  is equal to the quantity in parenthesis in (146). Comparing (147) with the more general equation (4),  $dq = c dT + l dv$ , we note that the quantity  $a$ , which is the specific heat at constant volume for mixtures of liquid and vapor, is a variable whose value can change between wide limits according to how much of the mixture is in the state of vapor.

**Difference of Specific Heats of Liquid and Vapor.**—The preceding equation (147) enables us to obtain a

useful expression for the difference between  $c$  and  $c'$  by means of an application of the second law of thermodynamics. Thus, dividing (147) by  $T$ , we obtain the exact differential

$$\frac{dQ}{T} = a \frac{dT}{T} + l \frac{dv}{T} \quad . \quad . \quad . \quad (i)$$

Then applying the usual operation to the second member, we have

$$\frac{1}{T} \frac{\delta a}{\delta v} = \frac{1}{T} \frac{\delta l}{\delta T} - \frac{l}{T^2} \quad . \quad . \quad . \quad (ii)$$

or

$$\frac{\delta a}{\delta v} = \frac{\delta l}{\delta T} - \frac{l}{T} \quad . \quad . \quad . \quad (iii)$$

but

$$a = c \frac{v'' - v}{v'' - v'} + c' \frac{v - v'}{v'' - v'}$$

hence  $\frac{\delta a}{\delta v} = \frac{c' - c}{v'' - v'}$ , and (iii) becomes

$$c' - c = \left( \frac{\delta l}{\delta T} - \frac{l}{T} \right) (v'' - v') \quad . \quad . \quad (iv)$$

but  $l(v'' - v') = L$ , hence (iv) may be written

$$c' - c = \left( \frac{dL}{dT} \right)_v - \frac{L}{T} \quad . \quad . \quad (148)$$

Further, if we combine (148) and (43), there results the useful equation

$$(c' - c) dT = dL - (v'' - v') dp \quad (149)$$

**General Expression for Change of Entropy.**—If we divide (144) by  $T$ , and eliminate  $c'$ , using its value as obtained in (148),

$$\frac{dq}{T} = ds = d\left(\frac{Lx}{T}\right) + c \frac{dT}{T} \quad . \quad . \quad (150)$$

Since  $c$  is nearly constant for ordinary liquids, (150) may be integrated, giving

$$s_p - s_{p'} = \frac{L_p x_p}{T_p} - \frac{L_{p'} x_{p'}}{T_{p'}} + c \log \frac{T_p}{T_{p'}} \quad (151)$$

by which we can easily calculate the change of entropy in passing from the point  $P$  to  $P'$  inside the saturation curve.

**Specific Heat of Saturated Vapor.**—The value of  $c'$  as found in equation (148), or  $c' = c + \frac{dL}{dT} - \frac{L}{T}$ , is most useful in this study of the specific heat of dry saturated vapor. The specific heat of a liquid,  $c$ , is, of course, always positive, though it is not quite constant, being a function of the temperature.  $\frac{dL}{dT}$  is always negative because  $L$  diminishes as the temperature rises, and becomes zero at the critical temperature. But  $L/T$  is, of course, always positive. Therefore  $c'$  can be either positive or negative according to whether, numerically,  $c >$  or  $< \frac{dL}{dT} + \frac{L}{T}$ . In the case of water vapor under ordinary conditions,  $c'$  is negative, while for ether vapor under similar conditions it is positive. In forming a mental picture of a negative specific heat, it is necessary to remember that in discussing the specific heat of dry saturated steam, we are restricted to a path along the dotted line that bounds the univariant region, on the vapor side, and to follow along such a path is a highly artificial process, in which temperature and pressure must be accurately adjusted to maintain the peculiar condition of simultaneous dryness and

saturation, that marks the limiting case we are discussing. Thus when  $c' < 0$ , it means that as we ascend this line toward higher temperatures we must simultaneously compress the vapor and withdraw heat, while the gain in temperature due to compression outweighs the loss due to this removal of heat.

**Graphic Representation of  $c'$ .**—Since  $dL/dT$  is always negative, and increases numerically very rapidly near the critical point, and moreover, since it has been found experimentally that  $c'$  increases with the temperature at points far below the critical, it follows from (148) that  $c'$  must decrease again at higher temperatures

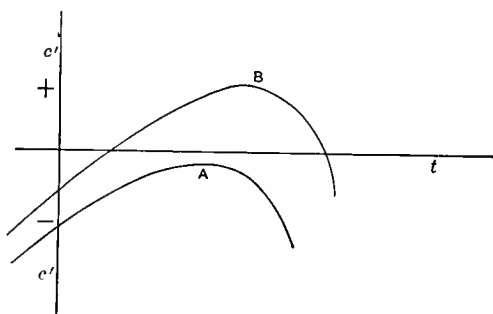


FIG. 30.

and so must pass through a maximum at some temperature lower than the critical. The maximum thus predicted may involve two reversals of the sign of  $c'$ , or none, as is evident from the curves in Fig. 30. The specific heat of saturated water vapor may follow a curve like *A*, and so be always negative; while sulphurous acid vapor gives a curve like *B* which is thus seen to change from negative to positive and back to negative again as the temperature rises.



**Dryness of the Mixture.**—We have hitherto regarded the region within the saturation curve as univariant. It is univariant with regard to those quantities that determine a system's thermodynamic condition. But if we introduce the quantity  $x$ , or "dryness," as it is often called, as a new variable, we can no longer regard the region as univariant, for we need to know two variables to completely define it, of which one may be  $x$ . This quantity varies between 0, when there is only liquid present, to 1 for dry saturated vapor, and is

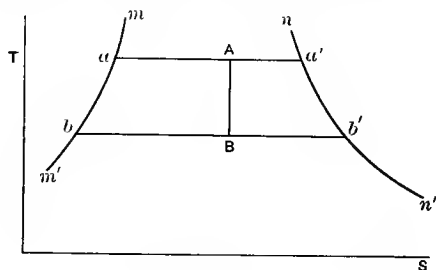


FIG. 31.

frequently referred to as a percentage. In order further to investigate  $x$ , we shall find the temperature-entropy diagram particularly useful. The curve  $m m'$  in Fig. 31 is the curve of the liquid at the boiling point, while  $n n'$  is the saturated vapor curve. Along these lines, a knowledge of either  $T$  or  $S$  is sufficient to determine the other, and consequently any other quantity as  $p$ ,  $v$ , etc., since these lines are strictly univariant. But in the region between them we must also know  $x$  in order to know all the characteristics of the mixture, such as its entropy, volume, etc., when  $T$  is given; or its temperature, when  $S$  is given. The relation between  $x$  and the entropy is

very simple, and can be expressed by setting  $dT = 0$  in the general entropy equation (150), or  $ds = d\left(\frac{Lx}{T}\right)$ . If the change is along an isothermal, then  $L/T$  is constant and we have, integrating,

$$s_1 - s_2 = \frac{L}{T}(x_1 - x_2) \quad . \quad . \quad . \quad (152)$$

Thus, as we proceed along any isothermal, as  $aa'$ , we gain in dryness in proportion as the entropy increases.

Consequently the dryness at any point  $A$  is  $\frac{aA}{aa'}$ .

**Critical Value of Dryness.**—Now suppose we start at a certain point  $A$ , whose dryness is  $x$ , and expand adiabatically to  $B$ , thus following a line of constant entropy. It is evident from the diagram (32) that the dryness at  $B$  is not necessarily the same as at  $A$ ; but it is possible to find a certain value of  $x$ , on a given isothermal  $aa'$ , such that an adiabatic expansion to  $bb'$  at a given lower temperature will leave the body in precisely the same state of dryness as it was before. That this must be possible, whatever the slope of the two curves, is clear from an inspection of the diagram. Let  $\xi$  be the critical value of  $x$ , then if  $x < \xi$ , there will be evaporation as a final result of expanding adiabatically to the new temperature, because the adiabatic will then tend to recede from the liquid curve; but if  $x > \xi$ , the final result will be a condensation instead. The value of  $\xi$  is readily found by a graphic method as follows: Draw  $aa'$  at the desired upper temperature and  $bb'$  at the desired lower temperature. Then construct chords through  $ab$  and  $a'b'$  till they intersect at  $P$ . Drop a perpendicular from  $P$  which divides

$a a'$  and  $b b'$  in proportional segments, then  $A$  is the point sought, and  $\frac{\overline{aA}}{\overline{aa'}} = \xi$ .

If the isothermal  $T'$  be made to approach  $T$  until it is infinitely close,  $B$  will finally coincide with  $A$ , at a point which has the curious property that an infinitesimal expansion does not result either in evaporation

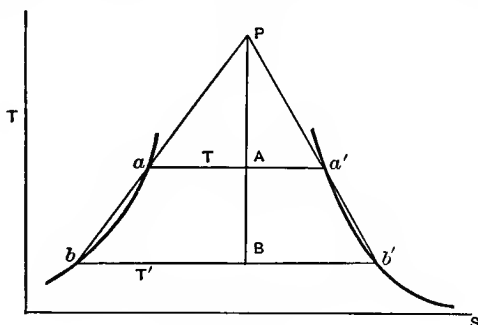


FIG. 32.

or condensation. There is one such point for every temperature, and an adiabatic expansion when  $x$  is less than this value must first result in evaporation; while an adiabatic expansion, when  $x$  is greater, results first in condensation. This initial evaporation or condensation, as the case may be, may change to the opposite process as the expansion progresses.

#### Changes in Dryness During Adiabatic Expansion.—

To find the amount of evaporation or condensation that results from a given adiabatic expansion or compression is a problem of great practical importance. In order to determine it for steam, we employ the approximation that the specific heat of water is constant,

and equal to unity, or  $c = 1$ . Hence the amount of heat required to raise the temperature of one gramme of water  $d T$  degrees is  $c d T = d T$ , and the change of entropy is  $d T/T$ . The change of entropy, due to complete evaporation is  $L_1/T_1$ , where  $L_1$  is the latent heat of vaporization at  $T_1$ . But if evaporation is incomplete, we must write instead  $x_1 \frac{L_1}{T_1}$  where  $x_1$  is the fraction evaporated. Therefore the total gain in entropy represented by heating water from  $0^\circ$  C. to  $T_1$  and then evaporating it to the state  $x$ , is given by

$$\int_{S_0}^{S_1} d s = \int_{T_0}^{T_1} \frac{d T}{T} + \frac{x_1 L_1}{T_1} \quad . \quad . \quad . \quad (i)$$

or integrated in full

$$s_1 - s_0 = \log \frac{T_1}{T_0} + \frac{x_1 L_1}{T_1} \quad . \quad . \quad . \quad (152')$$

A similar expression may be written for the change of entropy from  $0^\circ$  to a dryness  $x_2$  at a temperature  $T_2$ , but on the same isentropic as  $x_1$  (see Fig. 33), therefore, since  $s_1 = s_2$  by hypothesis we have

$$\int_{T_0}^{T_1} \frac{d T}{T} + \frac{x_1 L_1}{T_1} = \int_{T_0}^{T_2} \frac{d T}{T} + \frac{x_2 L_2}{T_2} \quad . \quad . \quad (ii)$$

which on integration becomes

$$\log T_1 - \log T_0 + \frac{x_1 L_1}{T_1} = \log T_2 - \log T_0 + \frac{x_2 L_2}{T_2} \quad (iii)$$

combining the terms there results

$$x_2 = \frac{T_2}{L_2} \left( \frac{x_1 L_1}{T_1} + \log \frac{T_1}{T_2} \right) \quad . \quad . \quad . \quad (153)$$

hence, if the initial temperature and dryness of the mixture are known, we can readily calculate the final

dryness after an adiabatic expansion to any desired temperature.

**Change in Intrinsic Energy.**—It is frequently desirable to calculate the difference between the intrinsic energy of a mixture of liquid and vapor, and the intrinsic energy

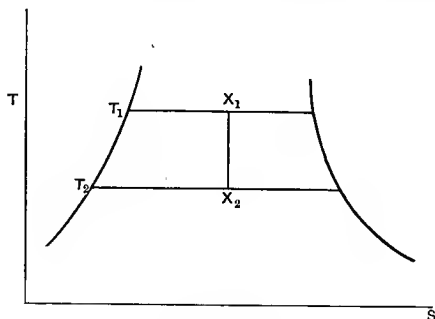


FIG. 33

of the same substance in the liquid state at some lower temperature, as for instance the freezing point of water.

Taking the defining equation for intrinsic energy  $du = dq - dw$ , we substitute for  $dq$  its value as given in equation (144), and for  $dw$  we can write  $p dv = p d[v'(1-x) + v''x]$ , therefore

$$du = L dx + c dT - cx dT + c' x dT - p dv' - p d(v''x - v'x) \quad (i)$$

where, as usual,  $c$  is the specific heat of the liquid and  $c'$  the specific heat of dry saturated vapor. Combining terms

$$du = L dx - p d(v''x - v'x) + (c' - c)x dT + c dT - p dv \quad (ii)$$

By equation (149)  $(c' - c) dT = dL - (v'' - v') dp$ , therefore, substituting for  $(c' - c) dT$  in (ii), we obtain

$$du = L dx + x dL - p d(v''x - v'x) - x(v'' - v') dp + c dT - p dv' \quad (iii)$$

or

$$du = d[Lx - px(v'' - v')] + c dT - p dv' \quad (154)$$

But  $d u$  is an exact differential, and regarding  $v'$  as constant, we may integrate the equation, obtaining,

$$u_1 - u_o = L_1 x_1 - p_1 x_1 (v'' - v') + \int_{T_o}^{T_1} c d T \quad (155)$$

The terms multiplied by  $x_o$  drop out, for the body was assumed to be wholly liquid at the lower temperature.

In this equation the two positive terms  $L x + \int_{T_o}^{T_1} c d T$  are the total heat supplied to the mixture from  $0^\circ \text{C.}$  to  $T_1^\circ$ ; from this is deducted the external work that was done against the pressure  $p$  when the liquid was vaporized to the dryness  $x_1$ , and the difference is obviously the net gain in intrinsic energy. The expression  $L + \int_{T_o}^{T_1} c d T$ , or  $H$ , is the heat required to raise one gramme of the liquid from  $0^\circ \text{C.}$  to  $T_1$  and completely vaporize it, and is commonly called the "total heat" of the vapor.

**Liquefaction of Gases.**—In liquefying the "permanent" gases, the principles we have just been discussing have a useful application. Air is usually liquefied by a method essentially due to Linde. In this machine the air is highly compressed and cooled, in order to withdraw the heat caused by the compression. It is then allowed to expand rapidly down to atmospheric pressure. In so doing its temperature falls, partly because of the work it does in overcoming the pressure of the atmosphere, and partly because of the Joule-Thomson effect, already discussed, which becomes increasingly important as the critical point is approached. The air, thus cooled

escapes by passing around the tube through which flows the air coming from the compressor, and as yet not fully expanded, and so chills it in advance. Thus the next quantity of air reaches a still lower temperature as a result of its expansion, and this *degenerative* process, as it might be called, ultimately lowers the temperature of the on-coming air below the critical point, so that further expansion results in condensation, as in the case of an ordinary vapor.

In considering the theory of Linde's machine, we have to take two stages into account. One in which the substance is bivariant and  $f(p, v, T) = 0$  applies; and later within the univariant region of saturated vapor where  $f(p, T) = 0$  applies.

If we assume that the expansion is essentially adiabatic we may write  $dq = du + dw = 0$ , hence  $du = -dw$ , or  $dw$  is an exact differential; and, as was shown in the last chapter, in the case of unresisted expansion, which applies roughly to Linde's machine,  $du + d(pv) = 0$ . It was further proved for the constant-volume gas thermometer (p. 128) that this equation may be transformed to  $c dT + l dv + v dp = 0$ , or, setting  $T \frac{\delta p}{\delta T} = l$ , we obtain

$$T \frac{\delta p}{\delta T} dv + c dT + v dp = 0. \quad (156)$$

Comparing this equation with (4), where  $dq = 0$  and  $T \frac{\delta p}{\delta T}$  is substituted for  $l$ , we see that (156) is not the equation of a true adiabatic, but it has a slope intermediate between an adiabatic and an isothermal on the  $p v$  diagram. It can only be plotted by assuming a

particular equation to represent  $f(p, v, T) = 0$ , such as Van der Waals' or Clausius'.

Now suppose the above expansion has carried the cooling down to the saturation curve of the gas in question, then a new state of things arises. The substance is defined by some function  $f(p, T) = 0$ . However, as before,  $du + d(pv) = 0$ , although  $du$  is no longer equal to  $c dT$ , but, as shown in equation (154), it is a more complicated function involving both the liquid and the vapor present in the mixture, or  $du = d[Lx - px(v'' - v')] + [c dT - p dv]$ , where the first term is the differential intrinsic energy of the vapor, and the second that of the liquid, as is readily seen by inspection, each being of the form  $dq - dw = du$ . But, since  $du = -d(pv)$ , we have

$$-d[pv'(1-x) + pv''x] = d[Lx - px(v'' - v')] + [c dT - p dv] \quad (157)$$

In which  $v'$ ,  $v''$  and  $c$  are functions of  $T$ . The solution of this equation, even approximately, is impossible, mainly because the function  $v'' = f(T)$  is unknown. If this were given, however, and  $v'$  and  $c$  were assumed constant, we might hope to calculate  $x$  from a knowledge of the ranges of temperature and pressure involved, and thus predict the quantity of air liquefied relative to the total amount cooled.

## ENERGETICS OF SATURATED STEAM

The practical problems involving the transformation of thermal into mechanical energy, using saturated vapor as the working substance, are almost invariably concerned with steam. Four kinds of steam expansion will be discussed; adiabatic, isothermal, isoenergetic (or at constant intrinsic energy), and one following the



saturation curve. During this discussion of saturated steam it should always be borne in mind that we are dealing with a univariant system as far as the steam proper is concerned, and we can always express one of these variables as a function of either of the other two. The most familiar of these possible general relations is  $p = f(T)$ , and tables or curves expressing it are of the greatest value. In other words, if we know the temperature of the saturated steam, the pressure is determined, and consequently its specific volume; and conversely, if the pressure is given, the temperature and specific volume may be found from the tables. Of course, if we are considering a mixture of steam and water (wet steam), the dryness becomes a second independent variable and complicates the problem, although it does not alter the relation referred to above, between  $p$  and  $T$ . It does, however, as is evident, enter into the calculation of the volume of the mixture as a whole.

**Adiabatic Work.**—In order to plot an adiabatic curve of saturated vapor on the pressure-volume diagram, we must know the relation between  $p$  and  $v$  for saturated steam, but unfortunately, like the relation of  $p$  to  $T$ , this is not known in analytic form. However, the following empirical equation, similar to (91) for perfect gases, has been found to correspond quite closely to the observed values for  $p$  and  $v$ . It is

$$p v^{\mu} = K \quad . \quad . \quad . \quad . \quad . \quad (158)$$

where  $K$  is a constant, and the exponent  $\mu$  depends upon the initial dryness of the steam. If the dryness  $x$  is known,  $\mu$  can be found from the empirical formula

$$\mu = 1.035 + .1 x \quad . \quad . \quad . \quad (159)$$

If the vapor is dry, obviously  $\mu = 1.135$ , which is seen to be considerably smaller than the exponent  $\kappa$  in the adiabatic equation for perfect gases. It is now possible to integrate the area under the adiabatic curve between two assumed values for  $v$ , assuming  $\mu$  constant over the range considered. This integration is effected as follows:

$$w = \int_{v_1}^{v_2} p \, dv \quad . \quad . \quad . \quad . \quad (i)$$

but by (158)  $p_1 v_1^\mu = p_2 v_2^\mu = p v^\mu$  hence

$$w = p_1 v_1^\mu \int_{v_1}^{v_2} \frac{dv}{v^\mu} \quad . \quad . \quad . \quad . \quad (ii)$$

$$w = \frac{p_1 v_1^\mu (v_2^{1-\mu} - v_1^{1-\mu})}{1-\mu} \quad . \quad . \quad . \quad . \quad (iii)$$

$$w = \frac{p_1 v_1 (1 - r^{1-\mu})}{\mu - 1} \quad . \quad . \quad . \quad . \quad (160)$$

where  $r$  is the ratio of expansion,  $v_2/v_1$ . Further, since  $p_1 v_1^\mu = p_2 v_2^\mu$  (iii) may be readily transformed to

$$w = \frac{p_1 v_1 - p_2 v_2}{\mu - 1} \quad . \quad . \quad . \quad . \quad (161)$$

(NOTE: These equations are made applicable to perfect gases by substituting  $\kappa$  for  $\mu$ ; (161) is readily converted to (95) by substituting  $RT$  for  $p v$ .)

Unfortunately,  $\mu$  varies so widely that these formulæ do not give accurate results with saturated steam; a better way, and the one commonly used, depends on the principle that the work done during an adiabatic expansion is at the expense of the intrinsic energy, or  $du = -dw$ . By equation (155),

$$u_1 = u_o + \int_{T_o}^{T_1} c \, dT + L_1 x_1 - p_1 x_1 (v'' - v')$$

But since  $v''$  is enormously greater than  $v'$  at any ordinary temperature, we may neglect  $v'$ , the volume of the water, as insignificant. The equation thus becomes

$u_1 = u_o + \int_{T_o}^{T_1} c \, dT + (L_1 - p_1 v'') x_1$ , where  $(L - p_1 v'')$  is the internal heat of vaporization at  $T_1$ . Set this equal to  $\rho_1$ , then at any other temperature  $T_2$ ,

$$u_2 = u_o + \int_{T_o}^{T_2} c \, dT + \rho_2 x_2$$

and the change of intrinsic energy between  $T_1$  and  $T_2$  is

$$u_1 - u_2 = \int_{T_2}^{T_1} c \, dT + \rho_1 x_1 - \rho_2 x_2 = A w \quad (162)$$

thus the work done during an adiabatic expansion is given in terms of the change of heat of the liquid, the internal heats of vaporization, and the initial and final dryness. As the problem is usually given  $T_1$ ,  $T_2$  and  $x_1$  are the conditions, then  $\rho_1$  and  $\rho_2$  as well as  $\int_{T_2}^{T_1} c \, dT$  are found in the steam tables, and  $x_2$  is calculated from equation (153).

**Isothermal Work.**—The work done during an isothermal expansion is more readily determined. Such an expansion in the case of saturated vapors always involves an increase in  $x$ , because if  $T$  is constant,  $p$  is constant also, therefore the increase of volume must mean the evaporation of some of the water present in the mixture.

Since  $p$  is constant,  $dw = p \, dv$  and  $v = v'' x + (1 - x) v' = v'' x$  very nearly, therefore  $dv = v'' \, dx$ , since  $v''$  is constant when  $T$  is constant, and  $dw = p v'' \, dx$  or

$$w = p v'' (x_2 - x_1) \quad . \quad . \quad . \quad (163)$$

Therefore if  $x_1$  and  $T$  are given we can find  $v''$  and  $p$  in the tables, calculate  $x_2$  from the known final conditions, and so find  $w$ .

**Isoenergetic Work.**—If the intrinsic energy is to remain constant during an expansion, it is obviously necessary to supply heat during the process. Since  $\Delta u = 0$ , (162) becomes

$$\int_{T_2}^{T_1} c dT + \rho_1 x_1 - \rho_2 x_2 = 0$$

If  $T_1$ ,  $T_2$  and  $x_1$  are known, we can calculate  $x_2$  from this equation. The curve representing this expansion is approximately an exponential of the form  $p v'' = \text{const.}$ , therefore  $p_1 v_1'' = p_2 v_2''$ , hence

$$v = \frac{\log p_1 - \log p_2}{\log v_2 - \log v_1} \quad . \quad . \quad . \quad (164)$$

To calculate  $v$ , we know  $p_1$  and  $p_2$  from  $T_1$  and  $T_2$ ; while  $v_1 = x_1 v''_1$ , and  $v_2 = x_2 v''_2$ , very nearly.

Finally, as in the case of the work done when  $p v'' = \text{const.}$ , we have like (161),  $w = \frac{p_1 v_1 - p_2 v_2}{v - 1}$ , where all the quantities are known.

**Work by Expansion of Dry Saturated Steam.**—A fourth interesting type of expansion is one in which the steam follows the curve of dry saturated vapor. The calculation is best performed with temperature and entropy as the variables, one of which is independent. As has already been explained, in reversible processes, enclosed areas on the  $T S$  diagram represent the quantity of heat transformed into work during the cycle represented by that area. But since  $J Q = W$ ,

such areas are proportional to the work done as well. In Fig. 34 the work done by the cycle  $A B C D$ , when the expanding steam follows the saturation curve be-

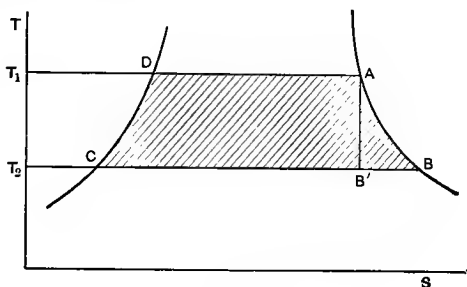


FIG. 34.

tween the temperature limits  $T_1$  and  $T_2$ , is given, for unit mass, by

$$w = \int_{T_2}^{T_1} s \, dT = \int_{T_2}^{T_1} \frac{L}{T} dT \quad . \quad . \quad . \quad (i)$$

But  $L$  has been shown to be approximately a function of the temperature (143), having the general form  $L = a - bT$ , where  $a$  and  $b$  are empirical constants. Therefore

$$w = \int_{T_2}^{T_1} \frac{a - bT}{T} dT$$

or integrating,

$$w = a \log \frac{T_1}{T_2} - b(T_1 - T_2) \quad . \quad . \quad (165)$$

Such an expansion, of course, involves the addition of heat from outside, since  $A B$  deviates from the adiabatic  $A B'$  in the direction of increasing entropy. If the expansion were adiabatic and the steam started initially dry at  $A$ , then at the end of the expansion  $x = \frac{DB'}{DB} < 1$ ,

at  $B$ . Therefore keeping the steam dry has cost a quantity of heat proportional to the area  $A B B'$ , or an increase in entropy equal to  $B B'$ . This added heat, however, results in some gain in useful work; although the transformation is at a lower efficiency than that of the original supply, because it is effected by "jacketing" the cylinder with "live" steam and the heat is supplied by conduction through the cylinder walls. Thus the heat represented by the area  $A B B'$  is supplied irreversibly and at temperatures lower than  $T_1$ , so its conversion into work is less efficient than that represented by the rest of the cycle.

**Carnot Cycle with Saturated Steam.**—The work done during a Carnot cycle, using saturated steam as the working substance, and operating between the temperatures  $T_1$  and  $T_2$ , and the drynesses  $x_1$  and  $x_2$ , is readily determined as follows: The efficiency of any reversible cycle is  $\frac{T_1 - T_2}{T_1}$ , hence the work done is the amount of heat absorbed during the isothermal expansion, multiplied by the efficiency. The quantity so absorbed is evidently  $L(x_1 - x_2)$ , where  $L$  is the latent heat at the temperature of the generator, hence the work is

$$w = \frac{J L (x_1 - x_2) (T_1 - T_2)}{T_1} \quad . \quad . \quad . \quad (166)$$

**Clausius Cycle.**—In the actual operation of the steam-engine, it is impossible even to approximate to the Carnot cycle, mainly because the heat is not supplied isothermally to the working substance, but is added at all temperatures between that of the feed water and that of the steam in the boiler. We may, however, de-

scribe a process known as the *Clausius cycle*, which corresponds to the ideal operation of an actual steam-engine, and, since it may be realized at least theoretically, forms a better standard of excellence than the wholly unattainable Carnot cycle.

In the Clausius process the water takes on heat at all temperatures between  $T_2$  and  $T_1$  with simultaneous increase of entropy and temperature. It is then evaporated isothermally at  $T_1$ . Next, as steam, it expands adiabatically to  $T_2$ , and finally is condensed isothermally at that temperature, and returned as water to the boiler to be heated over again. These steps may be shown graphically on the temperature-entropy diagram, Fig. 34, where  $CD$  represents the first step which obviously follows the liquid curve.  $DA$  is the isothermal expansion during vaporization.  $AB'$  is the adiabatic expansion, and  $B'C$  the isothermal condensation. The Carnot-cycle diagram would differ from this only in having an adiabatic compression take the place of  $CD$ , so that starting from a point on the  $T_2$  isothermal, directly under  $D$ , where the condensation is incomplete, the mixture would be brought to the wholly liquid state at  $D$ , without the addition of heat from outside.

It is easily seen that, although the Clausius cycle involves a larger area than the Carnot for the same temperature limits, it is less efficient; for even in the ideal case of complete reversibility, much of the heat is added at temperatures lower than  $T_1$ , thus involving a lower efficiency of converting into work the heat not supplied at  $T_1$ .

The calculation of the work done by unit mass of working substance operating in the Clausius cycle is

readily attained when the process is assumed to be reversible. During the first step, while the liquid is being heated from  $T_2$  to  $T_1$ , the available energy of the heat supplied is given by the product of that heat times the efficiency corresponding to the instantaneous value of the temperature; therefore,

$$A_{CD} = \int_{T_2}^{T_1} \left( \frac{T - T_2}{T} \right) c \, dT,$$

where  $T$  varies between  $T_1$  and  $T_2$ . Further, the available energy supplied during evaporation is given by

$$A_{DA} = L_1 \left( \frac{T_1 - T_2}{T_1} \right)$$

Therefore, the work performed during the complete cycle is

$$w = \int_{T_2}^{T_1} \left( \frac{T - T_2}{T} \right) c \, dT + L_1 \left( \frac{T_1 - T_2}{T_1} \right)$$

or

$$w = \int_{T_2}^{T_1} c \, dT - T_2 \int_{T_2}^{T_1} c \frac{dT}{T} + L_1 \left( \frac{T_1 - T_2}{T_1} \right)$$

Integrating with  $c$  taken as constant and unity in the second term

$$w = \int_{T_2}^{T_1} c \, dT - T_2 \log \frac{T_1}{T_2} + L_1 \left( \frac{T_1 - T_2}{T_1} \right) \quad (166')$$

This equation lends itself readily to numerical computation with the aid of steam tables, and remembering that the whole right-hand member must be multiplied by  $J$  to give  $w$  in joules. The efficiency may be computed by dividing  $w/J$  by  $\int_{T_2}^{T_1} c \, dT + L_1$ , which is the heat input, and then compared with that of the Carnot cycle operating between the same temperature limits.



**Non-expansion Cycle.**—Still another interesting cycle is that of an engine using steam non-expansively. In this case the cycle diagram is bounded by two lines of constant temperature, and two of constant volume. But isothermals for saturated steam are also constant pressure lines, hence the work done is represented on the  $p v$  diagram by the area of a rectangle whose sides are  $p_1 - p_2$  and  $v_2 - v_1$ ; therefore  $w = (p_1 - p_2)(v_2 - v_1)$ . If  $v_2$  is the volume of dry saturated steam, and  $v_1$  that of water, then

$$w = (p_1 - p_2)(v'' - v') \quad . \quad . \quad . \quad (167)$$

or

$$w = (p_1 - p_2) v'' \text{ nearly.}$$

**Fusion.**—Besides vaporization, two other changes of state exist known as fusion and sublimation. In fusion

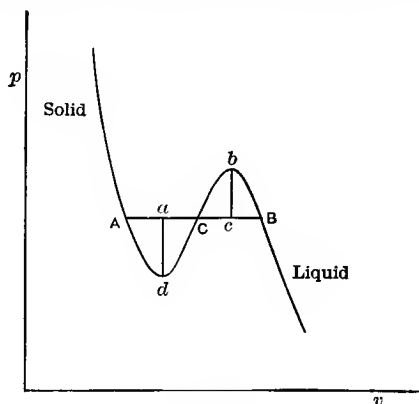


FIG. 35.

we pass from the solid to the liquid state, while the reverse process is known as freezing, or solidification. It is a reversible process under ordinary conditions,

and the isothermal of fusion is similar to that of vaporization. There are two points of discontinuity  $A$  and  $B$ , and a line of constant pressure between them as shown in Fig. 35. However, as in the case of vaporization, the curve is not necessarily discontinuous. If no "germs" of the solid, or other points that favor solidification, are present, the liquid may be made to follow the line  $Bb$ . This is not possible for the solid from  $A$  to  $d$ , but there are reasons for supposing that the curve may be regarded as continuous. At the points  $d$  and  $b$ , the change of state occurs abruptly and irreversibly, while the curve between these points represents an unstable condition which cannot be realized experimentally.

**Systems of Isothermals.**—In the case of most substances, fusion involves an increase of volume, and the

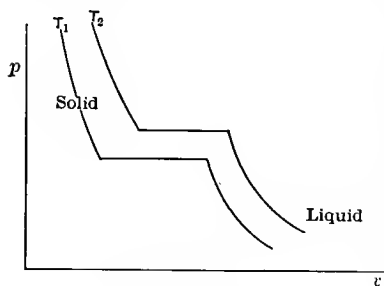


FIG. 36.

isothermals do not intersect, as shown in the diagram (36), but form a system in which those of higher temperature lie wholly above those of lower temperature. No critical temperature of fusion has ever been obtained, and the locus of the points

of discontinuity does not appear to belong to a closed curve as in the case of vaporization. Certain exceptional substances such as water show a decrease of volume during fusion. This brings the liquid branch of the isothermal curve to the left instead of the right of the diagram. A system of such isothermals must

intersect, as shown in Fig. 37, because increasing temperature, at constant pressure, in general causes an increase of volume, while it lowers the melting point of these exceptional bodies.

The points  $P$ , where they intersect, indicate that at a given pressure and volume it is possible to have the substance either all in one phase, or in a mixture of two phases in equilibrium with each other.

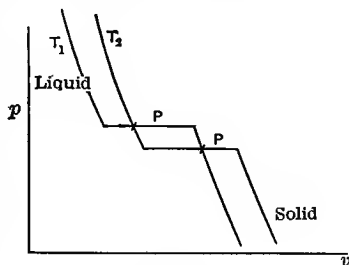


FIG. 37.

**Heat of Fusion.**—To represent the heat of fusion we may make use of a diagram in which  $Q$  and  $T$  are the coördinates. The abrupt change at constant temperature from  $A$  to  $B$  represents  $L$ , which, as is indicated in Fig. 38, changes with the temperature. In the

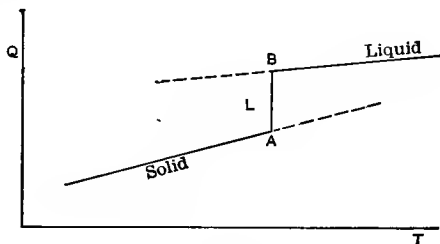


FIG. 38.

case of crystalline substances, the heat of fusion has a well-defined value at each temperature, but such bodies as glass and paraffine, which have no very definite melting point, have also no definite value of  $L$ . They may be regarded, however, as if melting followed a curve like

$A B$  in Fig. 39; thus  $L$  diminishes as fusion progresses, and they differ from crystalline bodies only in not melting at constant temperature.

**Sublimation.**—If we pass directly from the solid to the gaseous phase without the appearance of liquid, the process is called sublimation. It is theoretically possible with all substances at sufficiently reduced pressures,

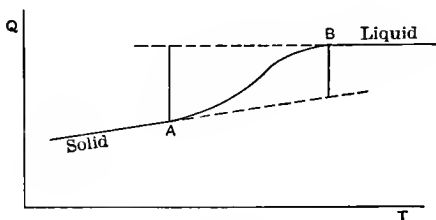


FIG. 39.

so that the liquid phase, at the temperature employed, cannot exist in a stable condition.

**Three-Phase Equilibrium.**—The relations that exist between fusion, vaporization, and sublimation are best shown on the pressure-temperature diagram.

The two diagrams, 40 and 41, show characteristic curves for both types of substance, represented by water on the one hand, and, say, mercury on the other. It will be seen that the three curves meet at the triple point, where all three phases may exist simultaneously in equilibrium. The region between the fusion and vaporization curves is one in which liquid alone can remain in equilibrium. Between the sublimation and fusion curves the substance is found only as a solid, in stable equilibrium, and between the vaporization and sublimation curves, only as a vapor. The curves are also shown

produced beyond the triple point to indicate the unstable condition that may be obtained by careful superheating or supercooling, as the case may be. Thus we may have water at  $-20^{\circ}\text{C}.$ , and a pressure corresponding

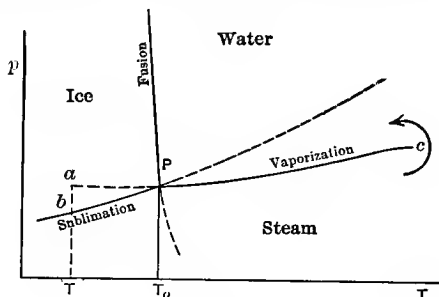


FIG. 40.

to the point  $a$ , in Fig. 40, which lies within the stable ice region. The potential of this supercooled water is such that any spontaneous change must lower it to that of ice,

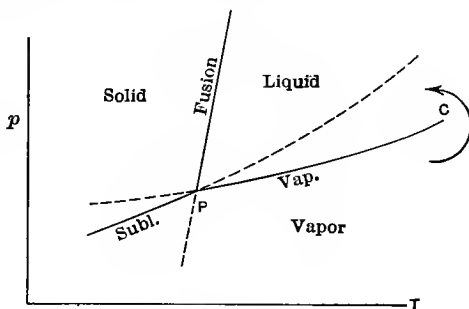


FIG. 41.

and it is, therefore, in an essentially unstable condition.

Following the method already made use of on p. 141, it is clear that at  $P$ ,  $F'_a = F'_b = F'_c$ , where the sub-

scripts denote the potentials of the solid, liquid, and gaseous states respectively. Further, along the fusion line,  $F'_a = F'_b$ , along the vaporization line,  $F'_b = F'_c$ , and along the sublimation line  $F'_a = F'_c$ . But solid and liquid in equilibrium (except at the triple point) have a potential less than that of vapor at the same pressure and temperature, because the vapor is unstable at such a point and tends to condense spontaneously, thereby indicating a higher potential; therefore along the fusion

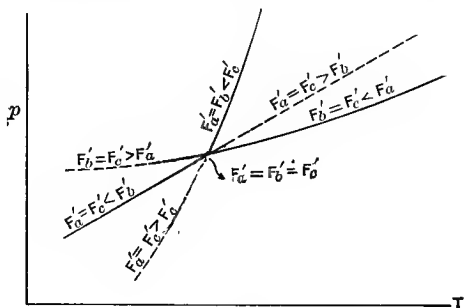


FIG. 42.

curve  $F'_a = F'_b < F'_c$ ; similarly the other two curves of stable equilibrium are such that  $F'_b = F'_c < F'_a$ , and  $F'_a = F'_c < F'_b$ . The dotted curves indicating the metastable condition are expressed by equations of the type  $F'_a = F'_b > F'_c$ , which applies to the fusion curve produced. This means that in the region indicated, the mixture of ice and water tends to vaporize spontaneously, thus indicating a higher potential than that of vapor at the same pressure and temperature. These results are shown collectively by Bryan, in a diagram similar to Fig. 42.

**Critical Temperature.**—The sublimation and fusion lines have never been explored far enough to find an end; but the vaporization line, as indicated, ends at the critical point *C*, and the diagrams 40 and 41 show clearly how it is possible to pass from liquid to vapor, or vice versa, without crossing the univariant region where both phases may exist simultaneously and where change of state takes place. A path such as that indicated by the curved arrow, means a passage from one state to the other, without experiencing any abrupt change such as vaporization or liquefaction.

**Transformations Near the Triple Point.**—An interesting difference between the two types of substances represented in Figs. 40 and 41 is the following: If we start with vapor at a low pressure and temperature, just above the triple point in Fig. 41, it is evident that by raising the pressure the substance will first become liquid, and then, at still higher pressures, solid. In the case of a substance like water, however, increasing pressure will produce the liquid, but the solid phase will not appear.

Again, if we take steam, at a temperature lower than the triple point, and raise the pressure, it passes directly into ice, and if the temperature is very near that of the triple point it will ultimately liquefy under very great pressure. But in the case of the other class of substances, the fusion curve slopes to the right, and a constant temperature line starting to the left of *P* can never intersect it, consequently the liquid phase will not appear, no matter how much the pressure is raised.

**Kirchoff's Formulæ.**—Using the formula of Clapeyron

we can write an expression for the "latent" heat that is involved in each change of state. Thus:

$$\left. \begin{aligned} L_1 &= T (v_2 - v_1) \frac{d p_1}{d T} \\ L_2 &= T (v_3 - v_2) \frac{d p_2}{d T} \\ L_3 &= T (v_3 - v_1) \frac{d p_3}{d T} \end{aligned} \right\} \quad . \quad . \quad . \quad (i)$$

where

$v_1$  = the specific volume of the solid at the triple point,  
 $v_2$  = the specific volume of the liquid at the triple point,  
 $v_3$  = the specific volume of the vapor at the triple point,  
 $p_1$  and  $L_1$  are the pressure and heat of fusion at  $P$ ,  
 $p_2$  and  $L_2$  are the pressure and heat of vaporization at  $P$ ,  
 $p_3$  and  $L_3$  are the pressure and heat of sublimation at  $P$ .

Now, suppose we pass around the triple point by an infinitely small reversible path, such that  $T$  is constant during the process. Then  $\int dQ = 0$  around this closed isothermal path, hence the algebraic sum of the heats is zero and  $L_1 + L_2 + L_3 = 0$ , but if the cycle is clockwise,  $L_1$  and  $L_2$  are positive while  $L_3$  is negative.

$\therefore L_1 + L_2 = L_3$  and equations (i) reduce to

$$(v_2 - v_1) \frac{d p_1}{d T} + (v_3 - v_2) \frac{d p_2}{d T} = (v_3 - v_1) \frac{d p_3}{d T} \quad (168)$$

A useful form of this equation which shows the relation between the slope of the sublimation and vapor curves is

$$\frac{d p_3}{d T} - \frac{d p_2}{d T} = \frac{v_2 - v_1}{v_3 - v_1} \left( \frac{d p_1}{d T} - \frac{d p_2}{d T} \right)$$

but  $v_3 - v_1$  is always positive,  $\frac{d p_2}{d T}$  is always positive,  $\frac{d p_1}{d T}$



has the same sign as  $v_2 - v_1$ , as was proved (p. 144), and has a greater absolute value than  $\frac{d p_2}{d T}$ , hence the right-hand member of the equation is always positive, so that  $\frac{d p_3}{d T} > \frac{d p_2}{d T}$ , which means that the sublimation curve is steeper than the vaporization curve, as was shown in the diagrams.

## CHAPTER VIII

### THE SOLUTION OF PROBLEMS

**General Remarks.**—There are two principal sources of difficulty in making numerical computations in thermodynamics. First: it is not always easy to decide on just the equation most suitable to the case in hand, and it may sometimes be necessary to modify some standard formula, or express it differently to meet an unusual situation. Second: in substituting numerical values in an equation, it is essential that the various quantities be absolutely congruent with regard to the units chosen, and the “dimensions” must harmonize on both sides of the equation; both are obvious but easily disregarded conditions. For instance, if  $p$  is expressed in pounds per square inch, then  $v$  should be given in cubic inches per pound; or if one side of the equation gives ergs and the other does not, it is evident that the equation is incorrect and some quantity such as  $R$  is needed to harmonize the dimensions. It may seem unnecessary to point out such obvious dangers, but it is the writer’s experience that nine errors out of ten, among beginners, come precisely from incongruent units, and inharmonious dimensions.

**Joule’s Equivalent.**—In using the equations of the preceding chapters, the student is again cautioned that  $J$  (or its reciprocal  $A$ ) is frequently omitted in the development of many important formulæ, and, in using any equation for quantitative work, he should make

sure that both members, if they deal with either heat or mechanical energy, are expressed in the same kind of units.

Joule's equivalent has no "dimensions," being a pure numeric, but it appears in all equations which connect heat with energy, and its value, of course, depends upon the system of units employed. For instance, if heat is expressed in terms of the ordinary calorie, and mechanical energy in joules, then  $J = 4.185$ . But if, instead, we use, as our heat unit, the average quantity necessary to raise a pound of water  $1^{\circ}$  F., between the limits of the freezing and boiling points, and the gravitational unit, or foot-pound, to express mechanical energy, then  $J$  becomes 777.9 nearly. The gravitational unit of energy is also used in the metric system; thus, taking the kilogramme-metre in place of the joule, the value of  $J$  becomes .4267. In Table I will be found values of  $J$ , or its reciprocal, for converting various units of one kind of energy into units of the other, and it will be found useful in numerical work.

**The Perfect Gas Constant,  $R$ .**—Another important constant whose value may be given in a variety of ways is the one which appears in the fundamental equation of perfect gases  $p v = R T$ . It has already been explained that  $R$  is ordinarily regarded as varying with the substance considered, and in each case depends upon the units chosen as well; but if a gramme molecule is taken as the unit mass, then  $R$  becomes a universal constant, though it still varies with the units chosen to measure the pressure and volume. If temperature is considered as having no dimensions, it is obvious that  $R$  has those of energy divided by mass and it may be expressed in

terms of ergs, calories, litre-atmospheres, etc., per gramme. Thus, if  $p$  is given in dynes per sq. cm. and  $v$  in cu. cm. per gramme, then  $pv$  = ergs per gramme, and, for a *gramme molecule* of any gas supposed "perfect,"  $R = 8.317 \times 10^7$  ergs/gramme-mol. This is readily reduced to the value corresponding to the gramme of a particular gas, by dividing by its molecular weight. If, however, the pressure is given in pounds per square foot, and the volume in cubic feet, while the temperature is on the Fahrenheit scale, then  $R = 1543$  ft. lbs. per *pound molecule* instead. Still another value is obtained by stating the pressure in terms of standard atmospheres, and the volume in litres, in which case  $R$  appears in terms of a unit known as the litre-atmosphere, being the work done by a pressure of one atmosphere acting on a square decimetre through a distance of one decimetre. Or, using the English system, we obtain the cubic-foot-atmosphere as the corresponding unit. Table II gives values for  $R$  per gramme molecule and pound molecule, according to several systems of units. It is, of course, understood that with the metric units, the temperature is Centigrade, and with the English units, Fahrenheit.

**Standard Conditions.**—The standard atmosphere, just referred to, is the pressure that will support a column of mercury 760 mm. high at  $45^\circ$  latitude, and mean sea-level, the thermometer being at the freezing point. This is 1,013,200 dynes/cm.<sup>2</sup>, or about 10,333 kg./M.<sup>2</sup>, and in the English system, about 14.696 lbs./in.<sup>2</sup>, or 2116.32 lbs./ft.<sup>2</sup> The standard temperature is  $0^\circ$  C., and for purposes of computation it is commonly taken as  $273^\circ$  on the absolute scale. The corresponding values Fahrenheit are  $32^\circ$  and  $492^\circ$ . The value of  $g$ , the

acceleration due to gravity, will be 980.6 cm./sec.<sup>2</sup>, which was adopted by the third Geneva Conference of Weights and Measures.

**Characteristic Constants.**—The quantities so far considered are, in a sense, universal, but most physical constants depend upon the nature of some particular body. Among the most important of these are density, and its reciprocal, specific volume, specific heat at constant pressure, and the heats of fusion and vaporization. From these quantities it is comparatively easy to calculate the values of the less familiar constants. Another group of characteristic constants are those that define the critical state, and derived from them the Van der Waals quantities  $a$  and  $b$ . There are also the quantities that determine a body's elastic properties, the coefficients or exponents of various types of expansion etc., etc. Tables III to VII inclusive, give various characteristics for certain selected bodies, and the succeeding problems will deal with the behavior of bodies included in these tables. Other constants not tabulated may be found, in most instances, quite readily from those that are given. For instance, the specific heat at constant volume is omitted in the tables, but is readily obtained from the value at constant pressure in a variety of ways. In the case of gases, where  $\kappa$ , the ratio of the specific heats, is known, we have only to divide  $C$  by this ratio to obtain  $c$ . Again, assuming the gas to be perfect, we may use equation (80)  $C - c = R A$ . If  $R$  is known for the gas in question, the process is evident. This would only be legitimate, however, when the gas closely approximates the hypothetical properties of perfect gases, as in the case of hydrogen at normal

pressure and temperature. In the case of liquids or solids  $c$  may be computed as follows: By (48) we find  $C - c = T \frac{\delta v}{\delta T} \frac{\delta p}{\delta T}$  but, by definition, the coefficient of expansion at constant pressure  $\alpha_p = \frac{1}{v} \frac{\delta v}{\delta T}$ , while, at constant volume,  $\alpha_v = \frac{1}{p} \frac{\delta p}{\delta T}$ . Substituting in (48),  $C - c = T p v \alpha_p \alpha_v$ . But  $\alpha_v$  cannot be directly observed, except for gases, hence we eliminate it by (17), or  $\alpha_v = \frac{\alpha_p E_T}{p}$ ; and finally, introducing Joule's equivalent, (48) becomes

$$C - c = A T v \alpha_p^2 E_T \quad . \quad . \quad . \quad (169)$$

where  $E_T$  is the modulus of elasticity at constant temperature. As an illustration, suppose the ratio  $\kappa$  is desired for glycerine at 20° C. and normal pressure. We find from the tables that the isothermal compressibility of glycerine,  $\frac{1}{E_T} = 25.1 \times 10^{-6}$ , measured in atmospheres, and  $\alpha_p = 5.05 \times 10^{-4}$ . The density = 1.262 = 1/v. In choosing a value for  $A$ , we must remember that  $v$  is given in cu. cm. per gramme, which is readily reduced to litres per gramme, while  $E_T$  is given in atmospheres; therefore referring to the Energy Conversion table, we find that a litre atmosphere = 24.21 gramme calories. Finally  $T = 293^\circ$ , at 20°. Inserting these values in (169), we obtain  $C - c = .0571$ . But  $C = .576$  for glycerine, therefore  $c = .519$  and  $\kappa = C/c = 1.11$  nearly.

## PROBLEMS FOR CHAPTER I

**The Heat Capacities.**—Numerous approximate computations may be made with the aid of the equations derived in the first chapter, provided the principal properties of the bodies considered have been sufficiently determined. Thus we may calculate the heat capacities of well-known liquids such as water or mercury from suitable equations taken from (5) to (13) inclusive. For instance, in the case of water and mercury, there are tables giving the specific volume for each degree of temperature over quite a wide range, thus we may obtain a small increment of volume  $\Delta v$  corresponding to an increment of temperature  $\Delta t$ , and assuming  $\frac{\Delta v}{\Delta t} = \left(\frac{dv}{dt}\right)_p$ , we can immediately compute  $\lambda$  from equation (12), with considerable accuracy, in terms of the known quantity  $C$ . By transposing (10) we have  $l = (C - c)\frac{\Delta t}{\Delta v}$  for finite increments, by which  $l$  is found, provided  $c$  has been computed by the method just indicated. Similarly, from the modulus of elasticity  $E_T$ , we have a value for  $\frac{\Delta v}{\Delta p}$ , and so may find  $h$  from equation (13),  $l$  being now known. Finally  $\eta$  is computed from (5) transposed, or  $\eta = (l - \lambda)\frac{\Delta v}{\Delta p}$ . The computation of the heat capacities of mercury follows:  $C = .0333$  at  $0^\circ \text{C.}$ ,  $c = .0280$  at the same temperature.  $\frac{\Delta v}{\Delta t}$  at  $0^\circ$ , from the tables of specific volume, taking an interval

from  $-10^\circ$  to  $+10^\circ$ , is  $\frac{1}{20} (.0734205 - .0736877) = .0000134$ .

$$\therefore \lambda = \frac{.0333}{1.34 \times 10^{-5}} = 2485$$

$$l = \frac{C-c}{1.34 \times 10^{-5}} = \frac{.0053}{1.34 \times 10^{-5}} = 395.5$$

$$h = l \frac{\Delta v}{\Delta p} \text{ where } \frac{\Delta v}{\Delta p} = \gamma_T v$$

$$\text{but } \gamma_T = -3.92 \times 10^{-6} (p \text{ in atmospheres})$$

$$v = .0735540$$

$$\therefore \frac{\Delta v}{\Delta p} = -3.92 \times 10^{-6} \times .073554 \text{ and}$$

$$h = -395.5 \times 3.92 \times 7.355 \times 10^{-8} = -1.114 \times 10^{-4}$$

$$\eta = (l - \lambda) \frac{\Delta v}{\Delta p} = 2089.5 \times 3.92 \times 7.355 \times 10^{-8} \\ = 6.0244 \times 10^{-4}$$

*Problem 1.*—Calculate  $\lambda$ ,  $l$ ,  $h$  and  $\eta$  for glycerine at  $20^\circ$  C. Take  $\gamma = -25.1 \times 10^{-6}$ ,  $\alpha_p = .000505$  (at  $20^\circ$  C.)

$$= \frac{1}{v} \frac{\Delta v}{\Delta t}, \text{ and } \rho = 1.2604$$

*Answer:*

$$\lambda = 1437.6$$

$$l = 142.26$$

$$h = -.0045007$$

$$\eta = .040969$$

*Thermoelastic Constants.*—The coefficient of cubical expansion at constant pressure,  $\alpha_p$ , and the coefficient of elasticity at constant temperature,  $E_T$ , or its reciprocal  $\gamma_T$  the compressibility, have been experimentally determined for most common substances, but  $\alpha_v$  can be



directly observed for gases only; so this quantity as well as  $E_S$ , the adiabatic modulus of elasticity, must be determined indirectly. To find  $\alpha_v$ , we have only to apply equation (17), where it is given in terms of  $\alpha_p$ ,  $E_T$ , and the pressure. Since  $E_T$ , or  $\gamma_T$ , are usually given in terms of atmospheres,  $p$  must be similarly stated. Thus for alcohol at  $10^\circ \text{C.}$ , and 10 atmospheres,  $\gamma_T = 92 \times 10^{-6}$ ,  $\alpha_p = .001101$ , therefore

$$\alpha_v = \frac{11.01 \times 10^{-4} \div 92 \times 10^{-6}}{10} = 1.197$$

$E_S$  is computed by aid of (17') or  $E_S = \kappa E_T$  where  $\kappa$  must be determined by the method applied to glycerine.

*Problem 2.*—Calculate  $\alpha_v$  and  $E_S$  for glycerine at  $20^\circ \text{C.}$ , and under a pressure of 6 atmospheres.

*Answer:*

$$\alpha_v = 3.35 \quad E_S = 4.42 \times 10^4$$

## PROBLEMS FOR CHAPTER II

The first and second laws of thermodynamics are seldom applied directly to numerical computations, but they are tacitly involved in nearly all thermodynamic problems. A direct application of the first law means simply the conversion of a quantity of energy expressed in heat units into the same quantity expressed in mechanical units, or vice versa; thus it is only necessary to apply the conversion factors given in Table I and use the two laws as stated in equations (22) and (26).

*Problem 3.*—How many foot-pounds are represented by 600 calories? How many B.T.U. are evolved by the complete conversion of 150 kg.-metres?

*Answer:* 1852.2 ft.-lbs. 1.395 B.T.U.

*Problem 4.*—A piston whose diameter is 20 cm. moves 10 cm. under a pressure of 10 atmospheres. How many calories of heat are transformed into work?

*Answer:* 760.68 gramme calories.

*Problem 5.*—In a certain thermodynamic transformation the working substance gains 600 calories of intrinsic energy, and 1,200 joules of work are done, how much heat must be supplied? What is the mechanical efficiency?

*Answer:* 886.68 gramme calories. 32.33 per cent.

*Problem 6.*—Twenty-five B.T.U. are consumed in heating a certain liquid-vapor mixture under a piston. The pressure exerted is 80 lbs. per sq. inch, the diameter is 1 ft. and the stroke 18 in. How much does the mixture gain in intrinsic energy? How great is the efficiency?

*Answer:* 7.553 B.T.U. 69.8 per cent.

*Problem 7.*—A Carnot engine takes 100 calories from the generator, and returns 80 calories to the refrigerator. How many ergs of work are done?

*Answer:*  $8.37 \times 10^8$  ergs.

*Problem 8.*—A Carnot engine, when run reversed, delivers 150 calories to the generator. If 300 joules are expended, how much heat was taken from the refrigerator?

*Answer:* 78.33 gramme calories.

*Problem 9.*—How much work, in joules, can an ideal engine perform, working between the temperatures of  $150^\circ$  C. and  $20^\circ$  C., if 180 calories are supplied at the higher temperature? What is the efficiency of the operation?

*Answer:* 231.5 joules. 30.73 per cent.

*Problem 10.*—An ideal engine operates with  $40^\circ$  F.

as its lower temperature. If it is capable of converting 3 B.T.U. into 400 ft.-pounds of work, what is the temperature of the generator?

*Answer:*  $143.4^{\circ}$  F.

*Problem 11.*—What must be the temperature of the refrigerator of an ideal engine if 1,500 calories at  $200^{\circ}$  C. are capable of raising a mass of 150 kg. a distance of 1.5 metres?

*Answer:*  $33.72^{\circ}$  C.

*Problem 12.*—An ideal engine receives 100 calories at  $120^{\circ}$  C., and rejects 80 calories to the refrigerator, what is the temperature of the latter?

*Answer:*  $41.4^{\circ}$  C.

*Problem 13.*—An ideal engine whose refrigerator works at  $10^{\circ}$  C., has an efficiency of 40 per cent. It is desired to raise this value to 50 per cent; how much must the temperature of the generator be raised? Or, how much must the temperature of the refrigerator be lowered?

*Answer:*  $94.34^{\circ}$  raised, or  $47.17^{\circ}$  lowered.

### PROBLEMS FOR CHAPTER III

In this chapter are considered entropy, potential, and available energy, apart from the properties of any particular body. Problems of a general nature dealing with these quantities can be solved because we are not concerned with their absolute values, but only with changes that may occur, and these changes are independent of the particular process followed, and may be expressed in terms of quantities that do not depend upon any especial substance.

**Entropy.**—Thus we may calculate the entropy gained

in supplying a certain quantity of heat at constant temperature by the simple ratio  $\frac{Q}{T}$ ; or the change of the entropy when  $Q_1$  heat units are supplied at  $T_1$ , and  $Q_2$  rejected at  $T_2$ , by the obvious statement  $S_1 - S_2 = \frac{Q_1}{T_1} - \frac{Q_2}{T_2}$ . Further, the gain of entropy of the working substance in a simple but irreversible engine, may be computed in general terms if the efficiency  $E$  is known, for the heat rejected is  $Q_1 - Q_1 E$ , and the entropy of this heat is  $\frac{Q_1(1-E)}{T_2}$  where  $T_2$  is the temperature at which the heat is rejected. Hence the entropy gained irreversibly is  $\frac{Q_1(1-E)}{T_2} - \frac{Q_1}{T_1}$ , where  $T_1$  is the temperature of the source.

**Availability.**—If the entropy, referred to some arbitrary zero, is given, the available portion of a quantity of heat follows from the defining equation of entropy, or  $Q E = Q - S T_2$ . The fundamental equation  $T dS = l W + dU$  may also be used for such general calculations, by writing  $T(S_1 - S_2) = \frac{\Delta W}{J} + U_1 - U_2$  since both  $dS$  and  $dU$  are exact differentials. Or we may make use of equations (31) to (34), remembering that  $dA$  is an exact differential as well as  $dU$ ; while  $T \Delta S = \Delta Q$ , and  $p \Delta V = \Delta W$  in reversible processes.

**Thermodynamic Potentials.**—The same is true of the equations  $dF_{TV} = dU - d(TS)$ , and  $dF_{PT} = dU + d(pV) - d(TS)$ , which may be integrated to  $F_1 - F_2 = U_1 - U_2 - (T_1 S_1 - T_2 S_2)$ , and  $F'_1 - F'_2 = U_1 - U_2 + \frac{(p_1 V_1 - p_2 V_2)}{J} - (T_1 S_1 - T_2 S_2)$ . And they readily

give the inner, and total thermodynamic potentials by writing  $T_1 = T_2$  in the first case; and  $T_1 = T_2$  and  $p_1 = p_2$  in the second case.

*Problem 14.*—A substance changes state at  $80^\circ$  C. by the addition of 500 calories, what is the gain in entropy?

*Answer:* 1.416.

*Problem 15.*—A substance changes state with the gain of 8 English entropy units, when 5,000 B.T.U. are supplied to it. What is the temperature of the transformation? *Answer:*  $165^\circ$  F.

*Problem 16.*—A substance at  $80^\circ$  C. receives 100 calories. At  $60^\circ$  C. it rejects 75 calories. What was the entropy gained? *Answer:* .058.

*Problem 17.*—In a certain engine, working between the limits of  $180^\circ$  C. and  $10^\circ$  C., the efficiency is 20 per cent. If the heat supplied is 90 calories, how much entropy is gained during the operation? *Answer:* .0557.

*Problem 18.*—An engine operates between  $300^\circ$  F. and  $40^\circ$  F. taking on 3,000 B.T.U. from the generator. If it gains one English entropy unit, what is its efficiency? *Answer:* 17.58 per cent.

*Problem 19.*—Seven hundred calories are supplied, with an absolute entropy value of 2. How much of the heat is available if  $0^\circ$  C. is regarded as the lowest available temperature? *Answer:* 154 calories.

*Problem 20.*—What is the maximum entropy with which 4,000 calories can be supplied, in order that an engine may do 4,000 joules of work; regarding  $20^\circ$  C. as the minimum temperature? *Answer:* 43.48.

*Problem 21.*—During the heating of a certain substance at  $60^\circ$  C., it expands, doing 40 joules of work, and

gains 8 calories of intrinsic energy. What is the gain of entropy? *Answer:* .0527.

*Problem 22.*—A substance receives 2 English entropy units at  $80^{\circ}$  F., and gains 200 B.T.U. of intrinsic energy. How many foot-pounds of mechanical work does it perform? *Answer:*  $6846 \times 10^2$  ft.-lbs.

*Problem 23.*—Calculate the gain in available energy of a system enclosed in a rigid envelope at the constant temperature of  $30^{\circ}$  C., when its intrinsic energy increases by 200 calories, with a loss of 1.5 entropy units. *Answer:* 654.5 calories.

*Problem 24.*—Calculate the change in available energy of a system under atmospheric pressure and at  $20^{\circ}$  C., when its intrinsic energy increases by 500 calories; its volume changes from 2 to 5 litres, and its entropy gains 2 units. *Answer:*  $-158.64$  calories.

#### PROBLEMS FOR CHAPTER IV

Very few of the equations derived in this chapter are capable of being used directly in calculations, although they are of the greatest value in obtaining workable expressions applied to such special substances as perfect gases, saturated steam, etc.

**Change of State.**—Maxwell's third relation as expressed in (43) is in a form available for numerical work, when  $\left(\frac{d\phi}{dT}\right)_v$  is regarded as being sensibly equal to  $\left(\frac{\Delta\phi}{\Delta T}\right)_v$ , or when it may be computed from some empirical equation connecting pressure and temperature; but these cases will be treated in full under the head of change of state to which they particularly belong.

**Heating by Compression.**—Maxwell's fourth relation gives us a means of making some computations of a quite general nature. By (45),  $h = -T \left( \frac{dv}{dT} \right)_p$  but during an adiabatic transformation (3) gives us  $\left( \frac{dp}{dT} \right)_q = -\frac{C}{h}$ . Substituting for  $h$  in (45) we obtain  $\frac{\delta p}{\delta T} = \frac{C}{T} \frac{\delta T}{\delta v}$  or  $\delta T = \frac{T}{C} \left( \frac{dv}{dT} \right)_p \delta p$ , but  $\alpha_p = \frac{1}{v} \left( \frac{dv}{dT} \right)_p$ , and finally, introducing Joule's equivalent, (45) becomes

$$\delta T = \frac{A T \alpha_p}{C} v \delta p \quad . \quad (170)$$

By means of this equation, taking finite increments, we may calculate, approximately, the change of temperature corresponding to a change of pressure at a given temperature, provided  $\alpha_p$  and  $C$  are known.

*Problem 25.*—Calculate the rise of temperature of carbon bisulphide when the pressure is increased from 1 to 20 atmospheres at  $18^\circ \text{C}$ . The density at that temperature is about 1.264. *Answer:*  $.529^\circ \text{C}$ .

**Cooling by Tension.**—Instead of compressing the body, it may be subjected to tension, in which case  $\delta p$  is negative. The formula just derived may be used to predict the cooling of a stretched solid provided it is assumed that the cross-section remains constant; hence  $dv = dl$  (where  $l$  is the length).  $\alpha_p$  must now be taken as the coefficient of linear expansion, and in place of  $v$ , we must introduce the *length* per unit mass.

*Problem 26.*—Assuming the cross-section to remain constant, and the process adiabatic, calculate the cooling

produced by a weight of 100 grammes hung on a copper wire whose diameter is 1.5 mm., where  $T = 20^\circ$ . Take  $\rho = 8.94$  and  $\alpha_p(\text{linear}) = 1.6 \times 10^{-5}$ . *Answer:*  $.419^\circ \text{C}$ .

## PROBLEMS FOR CHAPTER V

**Fundamental Equation for Perfect Gases.**—The combined laws of Boyle and Charles expressed by the familiar  $p v = R T$  are capable of immediate application to problems in which either  $p$ ,  $v$ , or  $T$  is unknown, and  $R$  has been determined for the gas in question.

As an illustration of this type of problem, suppose it is required to find the pressure, in atmospheres, when 15 grammes of nitrogen occupy two litres at a temperature of  $20^\circ \text{C}$ . Referring to Table III, we find  $R$  per gramme molecule, in terms of atmospheres and litres, is  $8.209 \times 10^{-2}$ . The molecular weight of  $N_2$  is 28.08, hence  $R$ , per gramme, is  $8.209 \times 10^{-2} \div 28.08$ , or  $2.923 \times 10^{-3}$ .

Now  $T = 293$  and  $v = \frac{2}{15}$  litre per gramme, therefore  $p = \frac{2.923 \times 10^{-3} \times 293 \times 15}{2} = 6.42$  atmospheres. Or we

may calculate  $R$  from the standard conditions of nitrogen. If  $p_o$  is the standard atmosphere,  $v_o$  the corresponding

specific volume at  $0^\circ$ , and  $T_o = 273$ , we have  $R = \frac{p_o v_o}{T_o} =$

$\frac{1 \times .79732}{273} = 2.921 \times 10^{-3}$ , which is a fairly close

agreement with the value obtained in the other way. The pressure may now be calculated as before. This latter method may be expressed in a single equation, for



since  $R = \frac{p_o v_o}{T_o}$ , we may write at once  $p = \frac{p_o v_o}{T_o} \times \frac{T}{v}$  which is perhaps the most convenient formula for this kind of problem.

Sometimes the mass is the unknown quantity. In this case we must substitute  $\frac{V}{m}$  for  $v$ , and, as  $V$  is given in such problems, the equation can be solved for  $m$ .

*Problem 27.*—Four lbs. of oxygen are subjected to a pressure of 500 lbs. per sq. in. at a temperature of  $60^{\circ}$  F. Calculate the volume. *Answer:* 1.392 cu. ft.

*Problem 28.*—How many grammes of hydrogen will occupy 5 litres under a pressure of 8,000 kg. per sq. metre, at  $25^{\circ}$  C.? *Answer:* .319 gramme.

*Problem 29.*—How great a pressure in lbs. per sq. in. will be needed to compress 10 oz. of air into a receptacle whose volume is 800 cu. in. at a temperature of  $-10^{\circ}$  F.? *Answer:* 225 lbs./in<sup>2</sup>.

*Problem 30.*—Fifteen grams of  $\text{CO}_2$  are in a vessel where the barometer reads 650 mm. The temperature is  $60^{\circ}$  C. What is the volume? *Answer:* 10.89 litres.

*Problem 31.*—The volume of a balloon contracts from 200 to 190 cubic yards at atmospheric pressure. The initial temperature was  $60^{\circ}$  F. What is the final temperature if no gas escaped? *Answer:*  $34^{\circ}$  F.

*Problem 32.*—If a reservoir holds 76 grammes of air under a pressure of one-tenth of an atmosphere at  $20^{\circ}$  C., how much will it hold under a pressure of  $2 \times 10^6$  dynes per sq. cm. at  $-10^{\circ}$  C.? *Answer:* 1671.3 grammes.

*Problem 33.*—Calculate the value of  $R$  for methane, carbon monoxide, and  $\text{NO}_2$  and so derive their specific volumes under standard conditions.

*Answer:*  $v_{\text{CH}_4} = 1.398$  litres/gramme.

$v_{\text{CO}} = .8004$  " "

$v_{\text{NO}_2} = .4868$  " "

**Heat Capacities of Perfect Gases.**—We have already considered the calculation of the specific heat at constant volume, when its value at constant pressure is known. The same methods apply, of course, to perfect gases, and the values so obtained are regarded as constant at all temperatures. The other heat capacities are readily computed from equations (78) to (83) and need no further comment except the caution that the units chosen must agree among themselves. To obtain values in the C. G. S. system,  $v$  should be expressed in cu. cm. per gramme and  $p$  in dynes per sq. cm.

*Problem 34.*—Calculate  $c$ ,  $\eta$  and  $\lambda$  for air,  $\text{H}_2$  and  $\text{O}_2$  under standard conditions, in absolute units.

<i>Answer:</i>	Air	Hydrogen	Oxygen
$c =$	.1693	2.418	.1542
$\eta =$	$4.56 \times 10^{-5}$	$6.51 \times 10^{-4}$	$4.16 \times 10^{-5}$
$\lambda =$	.0838	.0838	.0848

**Entropy, Intrinsic Energy, and Potential.**—The calculation of  $U$ ,  $S$ ,  $F$ , and  $F'$  is always made from some arbitrarily chosen zero. Thus, suppose it is desired to calculate the gain in entropy of a pound of air heated from  $10^\circ$  to  $100^\circ$  F., when the volume is doubled, we may apply formula (85) solving it for  $S - S_0$ ; when  $\frac{T}{T_0} = \frac{560}{470}$ , the last term becomes  $A R \log_e 2$ ;  $C/c = 1.4$ , and finally,  $S - S_0 = \frac{.24}{1.4} \log_e \frac{56}{47} + 1.29 \times 10^{-3} \times 53.18 \log_e 2 = .0773$ .

(NOTE.—In this, and in all other problems involving

logarithms, the Napierian are to be used, unless otherwise specified.)

To find the gain in intrinsic energy, or in the potential  $F'$ , proceed in a similar manner. In using (86) and (87) the term  $R T$  must be reduced to heat units as in the preceding case, by the factor  $A$ ; and the quantity  $S_0$  vanishes at the assumed zero of potential.

*Problem 35.*—Calculate the intrinsic energy, entropy, and potential  $F$ , of 20 grammes of oxygen at  $175^\circ \text{C}$ ., which is contained in a vessel of 5 litres capacity, where one atmosphere, and  $0^\circ \text{C}$ . are regarded as zero conditions.

$$\begin{aligned}\text{Answer:} \quad S - S_0 &= .2496 \\ U - U_0 &= 539.8 \text{ calories.} \\ F - F_0 &= 428.1 \text{ calories.}\end{aligned}$$

*Problem 36.*—Calculate the potential  $F'$ , referred to the same zero, of 15 grammes of  $\text{N}_2$  at  $240^\circ \text{C}$ ., under a pressure of 35 atmospheres. *Answer:*  $F' - F'_0 = 1975$  calories.

**The Thermoelastic Properties of Perfect Gases.**—The quantities  $\alpha_p$  and  $\alpha_v$  are both equal to the reciprocal of the temperature; while, as is well known,  $E_T = p$ , and they require no calculation.

**Heat of Expansion of Perfect Gases.**—The computation of the heat absorbed during the various types of expansion; or, conversely, that evolved during compression, is effected with the aid of (88), (89), or (90), according to the data given. The integration of each is perfectly obvious; for instance (88), when integrated, is  $q_1 - q_2 = c (T_1 - T_2) + (C - c) T_1 \log \frac{v_1}{v_2}$ . If preferred,  $R A$  may be substituted for  $C - c$  in the last term.

*Problem 37.*—Calculate the heat absorbed by 2 lbs. of air which expand from 20 cu. ft. at 60° F., to atmospheric pressure at the freezing point.

*Answer:* 5.728 B.T.U.

*Problem 38.*—Two grammes of air expand with the production of 8 joules of work, during which 10 calories of heat are absorbed. Calculate the change of temperature. *Answer:* 23.89° C.

*Problem 39.*—How much heat must be supplied to a quantity of gas, that it may perform one horse-power-hour of work by expanding at constant temperature? *Answer:* 2545.2 B.T.U.

**Adiabatic Expansion.**—When a gas expands adiabatically, the relation between pressure and volume is given by (92), where the second member is constant, and  $\kappa$  and  $R$  must be known for the gas in question. Many practical problems may be solved by its aid, and in general it is not necessary to compute the value of the constant, which may be set equal to  $K$  or any other symbol. Thus if the initial pressure and volume, and final pressure of a gas are given, while it is desired to find the final volume after adiabatic expansion, we have

$$p_1 v_1^\kappa = p_2 v_2^\kappa, \text{ or } v_2 = \left( \frac{p_1 v_1^\kappa}{p_2} \right)^{\frac{1}{\kappa}} = \left( \frac{p_1}{p_2} \right)^{\frac{1}{\kappa}} v_1.$$

*Problem 40.*—One kg. of hydrogen expands adiabatically from a pressure of 200,000 kg. per sq. metre, to 15,000 kg. per sq. metre. The initial volume was 150 litres; what is the final volume? *Answer:* 941.7 litres.

*Problem 41.*—Calculate the value of the exponent  $\kappa$  for a perfect gas, whose adiabatic curve passes through the points  $p_1 = 30$ ,  $v_1 = 2$ ,  $p_2 = 10$ , and  $v_2 = 4$ .

*Answer:* 1.585.

*Problem 42.*—In the preceding case, if  $C = .24$ , calculate  $c$  and  $R$  for the gas assumed.

*Answer:*  $c = .1514$ .

$R = .37078$  joules/gramme.

**Work Accomplished by Expansion.**—The work done during an isothermal expansion may be found from (97), where  $r$  may be either the ratio of the volumes or pressures; since, with  $T$  constant,  $r = \frac{v_2}{v_1} = \frac{p_1}{p_2}$ . The work of an adiabatic expansion may be readily computed from (95), or any of its derivatives, such as (95'). If  $p_1$  and  $p_2$  are given,  $v_1$  and  $r$  may be calculated from (91), and the work obtained as above.

*Problem 43.*—How much work is required to compress 3 lbs. of oxygen from 60 to 20 cubic ft., at a temperature of 40° F.? *Answer:* 79439. ft.-lbs.

*Problem 44.*—How much work is done when 6 kg. of CO<sub>2</sub> expand adiabatically from a temperature of 180° C. to 20° C.? *Answer:* 63.58 kg. m.

*Problem 45.*—How much work is done when 190 litres of nitrogen expand adiabatically from a pressure of 20, to 5 atmospheres? *Answer:* 311700. joules.

**Available Energy and Efficiency.**—The total available energy contained in a mass of compressed gas may be calculated from the same formulæ, either for adiabatic or isothermal expansion; but in each case we must deduct the energy wasted in expanding against the lower pressure of the process which, in practice, would be the atmosphere. Therefore the available energy

$W_A = W_T - p_2(v_2 - v_1)$ ; and the efficiency is  $1 - \frac{p_2(v_2 - v_1)}{W_T}$ ,

where  $W_T$  is the total energy represented by the compression from  $p_2$  to  $p_1$ . If the data are the initial and final pressures, the volumes may be found from  $p v = R T$ , or  $p v^\kappa = K$ , according to whether the expansion is isothermal or adiabatic; and the same two equations would be used if the volumes were given, and the pressures required.

*Problem 46.*—What is the available energy in a tank of 4 kg. of compressed air at 20 atmospheres, and  $15^\circ \text{C.}$ , if the expansion is to be carried down to one atmosphere, and at constant temperature? *Answer:* 675,950 joules.

*Problem 47.*—What is the available energy in a tank of 6 lbs. of compressed air at 30 atmospheres and  $60^\circ \text{F.}$ , if the expansion is to be adiabatic to one atmosphere? *Answer:* 199,870 ft.-lbs.

(This latter case is applicable when the expansion is very fast, while the former is true for very slow expansions. It may readily be shown that, when the expansion is conducted isothermally, the gas does more work, since it receives heat through the walls of the containing vessel.)

*Problem 48.*—Calculate the available energy in problem 47, assuming the expansion to be isothermal at  $60^\circ \text{F.}$ , and between the same pressure limits. *Answer:* 404,000 ft.-lbs.

**Change of Temperature During Adiabatic Expansion.**  
—The fall of temperature during an adiabatic expansion may be found directly from (96) in terms of the expansion ratio; or, eliminating  $v$ , by (91), which becomes

$$\frac{T_2}{T_1} = \left( \frac{p_2}{p_1} \right)^{\frac{\kappa-1}{\kappa}}$$

*Problem 49.*—What is the final temperature of a quantity of hydrogen, which expands adiabatically from a pressure of 6 atmospheres and  $30^{\circ}$  C. to 1.5 atmospheres? *Answer:*  $-70.5^{\circ}$  C.

*Problem 50.*—A quantity of air is compressed adiabatically so as to occupy one-tenth of its original volume; its temperature was  $20^{\circ}$  C. before compression, what is it afterward? *Answer:*  $468^{\circ}$  C.

**Closed Cycles with Perfect Gases.**—We now have to deal with the external energy involved when a perfect gas is put through a closed cycle of operations. In the cycles considered in this book, the calculation is perfectly simple. Thus, by (98), we find that the work per unit mass of working substance performed in a Carnot cycle, is given by

$$\omega = R (T_1 - T_2) \log r,$$

where  $r$  is the ratio of volumes of each adiabatic curve, and is greater than unity if the cycle is performed directly, but less than unity for the inverse process. If the initial and final pressures are given instead of the volumes,  $r$  may still be found, since  $T_1$  and  $T_2$  are known.

The constant pressure and constant volume cycle is still simpler, being given by  $\omega = \Delta p \Delta r$ . The Stirling cycle has the same equation as that of Carnot, but the ratio  $r$  refers to an isothermal, instead of an adiabatic expansion.

*Problem 51.*—Calculate the work done by 6 lbs. of oxygen regarded as a perfect gas, operating in a Carnot cycle between the temperatures of  $500^{\circ}$  F. and  $60^{\circ}$  F., and initial and final pressures of 200 and 15 lbs. per sq. in., respectively. *Answer:* 251,630 ft.-lbs.

*Problem 52.*—Calculate the external work in kg. metres when one kg. of perfect gas performs a rectangular cycle between the pressure limits of 8 and 1 atmospheres, and 10 and 3 cubic metres of volume. *Answer:* 506,317 kg. m.

*Problem 53.*—How much work is done per unit mass of working substance, by a Stirling engine using hydrogen, and operating between the temperatures of 150 C. and 10° C., and a volume ratio of 8? *Answer:* 1173.7 joules.

**Flow of Perfect Gases Under Pressure.**—In computing the velocity of flow, when a compressed gas escapes through an orifice, we may use equation (103) where the velocity is given in terms of quantities that are readily measured. It is, of course, essential that  $J$  should be expressed in suitable units. If  $u$  is to be given in cm. per sec. then  $J$  should be chosen so as to reduce calories to ergs, while if  $u$  is in ft. per sec.  $J$  must reduce B.T.U to ft.-poundals.

*Problem 54.*—Nitrogen gas, under a pressure of 20 kg. per sq. cm., and at 18° C., is allowed to escape into the atmosphere. What is the velocity of flow, if the process is regarded as adiabatic and without friction? *Answer:* 585.6 m/sec.

*Problem 55.*—Compressed air escapes from a receiver into the atmosphere with a speed of 2,000 ft. per sec. The initial pressure was 20 atmospheres, what was the temperature, assuming the process to have been adiabatic and without friction? *Answer:* 123° F.

**Estimation of Altitudes.**—Either (106) or (106') may be used to estimate the heights of mountains with the barometer, though the latter is more correct, especially



at great altitudes. Of course  $R$  must be expressed in terms of ergs per gramme, and  $g$  in cm. per sec.<sup>2</sup> to give  $h$  in cm.; or in the English system,  $R$  must be in foot-pounds per pound and  $g$  in ft. per sec.<sup>2</sup> to give  $h$  in feet.

*Problem 56.*—Assuming the atmosphere isothermal, calculate the height of a mountain when the barometer read 560 mm., while at sea level it stood at 760 mm., with a temperature of 18° C. *Answer:* 2598. metres.

*Problem 57.*—Calculate the height of the same mountain assuming the atmosphere adiabatic. *Answer:* 2481. metres.

## PROBLEMS FOR CHAPTER VI

**Van der Waals' Equation.**—Real gases are most readily dealt with by aid of this celebrated equation. For purposes of computation we may transform it to read  $(p + \frac{a}{v^2})(v - b) = 1 + \frac{t}{273}$  where  $t$  is the temperature in degrees Centigrade and  $p$  and  $v$  are no longer specific pressure and volume, but the pressure is measured in atmospheres, and the volume in terms of the *normal specific volume* of the body in question taken as unity. This normal specific volume means the volume one gramme of the substance would occupy at 0° C., and under atmospheric pressure, provided it behaved like a perfect gas at that temperature. Now the specific volume of a gramme molecule of a perfect gas at 0°, and under the pressure of one atmosphere, is 22.41 litres, therefore the normal specific volume in litres is equal to 22.41 divided by the molecular weight of the substance in question. It is thus possible to find  $v_0$  for bodies that are really liquid at the freezing point.

Adopting these units, it is obvious that  $R = \frac{p_o v_o}{T_o} = \frac{1}{273}$  therefore  $T R$ , which is the second member of Van der Waals' equation, becomes  $\frac{T}{273}$ , which may be written  $1 + \frac{t}{273}$ . The quantities  $a$  and  $b$ , based on the scale of pressures and volumes assumed above, have been calculated for a great variety of substances from their observed critical pressures and temperatures. We saw in the paragraph on the critical point, that the critical temperature  $T_c = \frac{8a}{27bR}$  and the critical pressure  $p_c = \frac{a}{27b^2}$ . From these equations are readily derived  $a = \frac{27R^2 T_c^2}{64 p_c}$  and  $b = \frac{R T_c}{8 p_c}$ . But since  $R = \frac{1}{273}$ , they reduce to

$$a = \frac{27 T_c^2}{64 \times 273^2 \times p_c} \text{ and } b = \frac{T_c}{8 \times 273 \times p_c}$$

Table VI gives values for  $T_c$  and  $p_c$ , as well as  $a$  and  $b$ , for several gases, and substances liquid under ordinary conditions. The latter quantities have been computed from the former, as indicated above, and are taken from Landholt and Börnstein's Tables. The values chosen are by those observers who seemed to agree most nearly with the mean of all.

**Isothermal Curves.**—We are now in a position to plot the isothermal of a body supposed to be described by Van der Waals' equation. For instance, in the case of  $\text{CO}_2$ , equation (107) becomes

$$p_1 = \frac{-.00683}{v^2} + \frac{T}{273(v-.001813)}.$$

Now let  $T$  have any assumed value, as 273, or the critical temperature  $273 + 31.9$ , and then  $p$  may be computed for a series of values of  $v$ .

*Problem 58.*—Plot the isothermal of ether at  $60^\circ$  C., also the critical isothermal.

**Entropy.**—By equation (113) we may readily calculate the entropy of a Van der Waals body  $S - S_0$ , above any chosen zero, and for an assumed temperature and specific volume. In this problem  $c$  must be known approximately for the range of temperature involved,

$b$  is taken from the tables,  $R = \frac{1}{273}$ ,  $v_0 = 1$ , and  $v$  is to be expressed in terms of  $v_0$ . Finally the last terms, in which  $R$  appears, must be multiplied by the constant  $A$  expressed so as to transform into calories our new mechanical unit,  $v_0$ -litre-atmospheres, where  $v_0$  is the normal specific volume given in litres. Thus for oxygen,  $A = \frac{22.41 \div 32}{.0413}$ , where the numerator is the value of

$v_0$ , and the denominator the suitable value of  $J$  taken from the energy conversion table.

*Problem 59.*—Assuming atmospheric pressure and freezing point as the entropy zero; calculate its value in 4 grammes of ammonia at  $80^\circ$  C., when enclosed in a receiver whose capacity is 5 litres. *Answer:* .407.

**Intrinsic Energy.**—By means of (114) we may calculate the gain of intrinsic energy,  $u - u_0$ , above any assumed zero. Here the quantities are measured as above, and the last term must be reduced to calories by

the factor  $A$ , because  $\frac{a}{v^2}$  has the dimensions of a pressure, hence  $a \left( \frac{v-v_0}{v v_0} \right)$  has the dimensions of  $p v$ , or mechanical work.

**Problem 60.**—Calculate the intrinsic energy, assuming the same zero as above, for 9 grammes of  $\text{CO}_2$ , at  $18^\circ \text{C}$ ., contained in a receiver whose capacity is 3 litres.  
*Answer:* 26.82 gramme calories.

**Thermodynamic Potential.**—In applying (115) to calculate  $f - f_0$ , it is obvious that the last two terms of the right-hand member must be multiplied by  $A$ , the value being the same as in the preceding cases.

**Problem 61.**—Calculate the potential  $F$  of 6 grammes of nitrogen at  $10^\circ \text{C}$ ., in a receiver whose capacity is 750 c.c. *Answer:* 243.2 calories.

**Heat Capacities  $l$  and  $h$ .**—These values may be found from (116) and (117) multiplied by  $A$ .

**Problem 62.**—Calculate  $l$  and  $h$  for ammonia at  $100^\circ \text{C}$ ., and a specific volume of .2 litre per gramme.

$$\text{Answer: } \begin{aligned} l &= 9.0696 \times A \\ h &= .003498 \times A \end{aligned}$$

**Specific Heat at Constant Volume.**—Here we have only to apply (118), provided  $C$  is known, and solve for  $c$ . The right-hand member must, of course, be multiplied by  $A$  adapted to  $v_0$ -litre-atmospheres of the gas considered, and as usual,  $R = \frac{1}{273}$ .

**Problem 63.**—Assuming the specific heat at constant pressure of  $\text{CO}_2$  to be .1843 at  $0^\circ$  and atmospheric pressure, calculate  $c$  under the same conditions. Also cal-

culate  $c$  when the pressure is such that at  $0^\circ \text{C.}$ , 5 grammes occupy 400 c.c. *Answer:* (a) .1385; (b) .1349.

**Thermoelastic Coefficients.**—Although the equations have not been derived in the text, it is not difficult to calculate the thermoelastic coefficients by aid of equations (66), (67), and (68). Thus, to determine  $E_T$  from equation (115), we have

$$\left(\frac{df}{dv}\right)_T = \frac{a}{v^2} - \frac{TR}{v-b}, \text{ and } \left(\frac{d^2f}{dv^2}\right)_T = -\frac{2a}{v^3} + \frac{TR}{(v-b)^2},$$

hence

$$E_T = -\frac{2a}{v^2} + \frac{TRv}{(v-b)^2} \quad \cdot \quad \cdot \quad \cdot \quad (171)$$

Similarly we may obtain  $\alpha_p$ , for

$$\begin{aligned} \left(\frac{df}{dT}\right)_v &= -R \log \left(\frac{v-b}{v_0-b}\right) \\ \frac{\delta^2 f}{\delta v \delta T} &= -\frac{R}{(v-b)} - s_0 \end{aligned}$$

but by (68)

$$\alpha_p = -\frac{\delta^2 f}{\delta v \delta T} \bigg/ v \frac{\delta^2 f}{\delta v^2}$$

hence

$$\alpha_p = \frac{Rv^2(v-b)}{RTv^3 - 2a(v-b)^2} \quad \cdot \quad \cdot \quad \cdot \quad (172)$$

Thus, if  $v$  and  $T$  are given, we may find  $\alpha_p$  in terms of known constants.\* Finally by (66)

$$\alpha_v = \frac{\delta^2 f}{\delta v \delta T} \bigg/ \left(\frac{df}{dv}\right)_T$$

or

$$\alpha_v = \frac{Rv^2}{RTv^2 - a(v-b)} \quad \cdot \quad \cdot \quad \cdot \quad (173)$$

In the case of certain bodies such as hydrogen,  $a$  is so much smaller than  $b$ , that it may be neglected in com-

parison. In such cases the thermoelastic coefficients reduce to

$$E_T = \frac{T R v}{(v-b)^2}$$

$$\alpha_p = \frac{R (v-b)}{R T v}$$

$$\alpha_v = \frac{1}{T}$$

and if  $b$  is regarded as negligible, we recover the values for perfect gases, or  $E_T = p$  and  $\alpha_p = \alpha_v = \frac{1}{T}$ .

But this is far from justifiable, even in the case of hydrogen, for both  $\alpha_p$  and  $\alpha_v$  vary considerably with the pressure (and consequently volume), although the latter quantity is less dependent on it than the former, as the above results indicate. Table VII gives some values for  $\alpha_p$  and  $\alpha_v$  determined by Amagat, and taken from Ewell's "Physical Chemistry."\* The anomalous behavior of hydrogen, which has already been referred to, is evident when we compare the steady decrease of  $\alpha_p$  as compared to the increase toward a maximum, followed by a decrease, in the case of other gases.

*Problem 64.*—Calculate  $E_T$ ,  $\alpha_p$  and  $\alpha_v$  for  $\text{CS}_2$  at  $0^\circ \text{C}$ ., and normal specific volume. *Answer:*  $E_T = .9628$ .

$$\alpha_p = .003817.$$

$$\alpha_v = .003745.$$

*Problem 65.*—Calculate the same quantity for  $\text{N}_2$  at  $-80^\circ \text{C}$ ., and a specific volume .025 normal.

$$\text{Answer: } E_T = 3.0358.$$

$$\alpha_p = .006499.$$

$$\alpha_v = .006333.$$

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\* Published by P. Blakiston's Son & Co.

*Problem 66.*—Calculate the same quantities for  $\text{CO}_2$  under standard conditions of pressure and temperature, and compare results with the table.

$$\text{Answer: } E_T = .98998.$$

$$\alpha_p = .003707.$$

$$^*\alpha_v = .003688.$$

**Work Done by Expansion.**—When a Van der Waals body expands with the performance of external work, there are the two principal cases of isothermal and adiabatic expansion to be considered. Equation (119) relates to the former case, and gives us the work per unit mass in terms of the temperature of the expansion, the initial and final volumes, and the characteristic constants  $a$  and  $b$ . Joules' equivalent does not appear in the equation, for both terms are in mechanical units; but if  $v$  is expressed in terms of  $v_o$ , and  $a$  and  $b$  are taken from Table VI, then, instead of joules,  $w$  will be given in  $v_o$ -litre-atmospheres, and must be reduced to joules by dividing by  $9.869 \times 10^{-3}$  (see energy conversion table), and multiplying by  $v_o$ , as in the cases already considered.

*Problem 67.*—How much work is done by 6 grammes of oxygen expanding isothermally at  $40^\circ \text{C.}$ , from 1.5 to 5 litres? *Answer:* 575.3 joules.

Adiabatic work is calculated with equal ease by (120); but, as in the case of equation (119), the second term must be reduced to joules. If  $\kappa$ , the ratio of the specific heats of the gas in question, is known, we may determine  $c$  from a value of  $C$  appropriate to the conditions assumed; otherwise  $c$  must be computed from (118).

If  $T_1$ ,  $T_2$ ,  $v_1$  and  $v_2$  are all given, the calculation is obvious, but if any one of these quantities is not known,

we may get an approximate value from (96), assuming that the expansion curve is given by  $p v^{\kappa} = K$ , as for perfect gases.

**Problem 68.**—How much work is done when 15 grammes of hydrogen expand adiabatically from a temperature of  $100^{\circ}\text{C.}$ , and a volume of 2 litres, to a volume of 10 litres? *Answer:* 13,502 joules.

**Carnot's Cycle.**—If the gas passes through a Carnot cycle, equation (121) gives the work done per gramme. The right-hand member is in mechanical units, but must be reduced to joules as has been explained. In such problems, we must know  $T_1$ ,  $T_2$  and three out of the four volumes. The remaining volume is found by the perfectly general property of Carnot's cycle  $\frac{v_2}{v_1} = \frac{v_3}{v_4}$  which was stated in the chapter on perfect gases. If only one of the temperatures is given, or only two of the volumes, the missing quantity may be estimated by (96), which is, however, not rigorously true for real gases.

**Problem 69.**—How much work is done when 2 grammes of  $\text{CO}_2$  perform a Carnot cycle, where  $t_1 = 150^{\circ}\text{C.}$ ,  $t_2 = 40^{\circ}\text{C.}$ ,  $V_1 = 200\text{ c.c.}$ , and  $V_2 = 400\text{ c.c.}$ ? *Answer:* 34.31 joules.

**Clausius' Equation.**—The application of this equation is more difficult than that of Van der Waals, not only because it is more complicated, but because it involves three constants besides  $R$ , and thus requires the determination of three critical values instead of two, if its constants are to be calculated. From equations (124), (125), and (126), it is evident that  $v_c$ ,  $T_c$  and  $p_c$  must all be known to solve for  $\epsilon$ ,  $B$  and  $D$ ; and unfortunately  $v_c$  has been observed for only a few substances. In the



case of  $\text{CO}_2$ , Clausius found the following values for the constants that appear in his equation:

$$\begin{aligned} D &= 2.09 \\ B &= .00095 \\ \epsilon &= .00087 \end{aligned}$$

expressed in terms of atmospheres and  $v_0$  as unit of volume; while  $R = \frac{1}{273}$  as in the preceding case. We are now in a position to calculate  $u$  from equation (128) and, using  $u$  as a basis, it is possible to determine the various other quantities, exactly as  $f$  was used, in investigating a Van der Waals body. We shall, however, not undertake the task, on account of the rather limited numerical data available.

**Cooling by Unresisted Expansion.**—Equation (135) may be used in connection with  $\text{CO}_2$  to estimate the cooling during unresisted expansion. In using this equation, we must reduce the right-hand member to calories, remembering that it yields  $v_0$ -litre-atmospheres, provided the values for  $D$  and  $\epsilon$  just given are used.

*Problem 70.*—Calculate the fall of temperature when  $\text{CO}_2$  at  $27^\circ \text{C}$ . expands unresisted from a pressure of 2 atmospheres into the air at normal pressure. *Answer:*  $1.33^\circ \text{C}$ .

(NOTE.—Joule and Kelvin found  $1.15^\circ$  by experiment.)

## PROBLEMS FOR CHAPTER VII

There are two changes of state of especial importance, namely fusion and vaporization. Problems dealing with the former are comparatively simple, and may be readily solved by practically the same methods and equations

that are applicable to the more difficult case of vaporization. We shall, therefore, proceed at once to explain the solution of problems which involve the transformation of liquid to vapor, and the properties of saturated vapor. Water, being the substance most commonly used in the practice of thermodynamics, has been studied more completely than any other substance; so the discussion will mainly be confined to the behavior of water in the states of liquid and steam, and mixtures of both.

**Steam Tables.**—Practically all problems of this kind demand the use of steam tables in which values of various quantities are set down corresponding to an ascending scale of temperatures, or of pressures. A typical table of this sort is that of C. H. Peabody which has been used in the solution of the problems under this head. We find there for each degree of temperature of steam, the following quantities worked out, in most cases, to four significant figures. 1. The vapor tension of the steam, in terms of the barometer reading (inches or millimetres), or in pounds per sq. inch. 2. The heat required to raise water from freezing point to the temperature in question. 3. The heat of vaporization,  $L$ . 4. The value of that portion of  $L$  which is concerned in changing the internal structure of the water during vaporization, called "heat of internal work." 5. The value of the remaining portion of  $L$  which does external work against the existing pressure, called "heat of external work." 6. The entropy of the liquid taken from freezing to the given temperature. 7. The entropy of vaporization. 8. The specific volume of the steam. 9. The density of the steam.

**Calculation of Steam Tables.**—The preceding quanti-

ties are calculated as follows: Considering the metric table (both English and metric tables are given), we have first the pressures to determine in terms of the temperatures. In Peabody's revised tables these values are based mainly on the experimental observations of Holborn and Henning published in 1908. The heat of the liquid, in the case of water, is found by writing  $c = 1 + k$ , where  $k$  is the small difference between the specific heat and unity; therefore the heat of water above  $0^\circ$  C. is given by  $t + \int_{t_0}^t k \, dt$ . Since  $k$  is always small, this may be integrated graphically with sufficient precision, making use of the known values of  $k$  taken for the range considered.

The heat of vaporization may be found for any temperature by some formula such as (143). A more recent one, due to Henning, and used by Peabody, is  $L = 94.210 (365 - t)^{.31249}$

We may separate the internal from the external portion of  $L$  by (139), thus obtaining the next two quantities, No. 4 and No. 5. The entropy of the liquid is calculated by means of the integral  $\int_{t_0}^t c \frac{dt}{T}$ , where  $c$  is set equal to  $1 + k$  as before. Therefore the entropy becomes equal to  $\log_e \frac{T}{T_0} + \int_{t_0}^t k \frac{dt}{T}$ . The first term is readily computed, and the second is evaluated graphically by a method similar to that used in obtaining the heat of the liquid. The entropy of vaporization is obtained directly from  $L$ , by dividing by the absolute temperature at which it occurs.

Finally, to find the specific volume and the density, its

reciprocal, at the temperature  $T$ , we use the equation of Clapeyron in the form of (43). Here  $L$  is already known,  $v_2$  is the volume sought, and  $v_1$  is the specific volume of water at  $T^\circ$ , which is known with sufficient accuracy, considering its smallness compared to  $v_2$ . We may determine  $\frac{d p}{d t}$  with considerable precision, in the case of steam, by taking small finite increments  $\Delta p$  and  $\Delta t$ , and finding that value of  $\Delta p$ , from the tables, which corresponds with the temperature interval assumed. This interval should be taken from a temperature slightly below, to another slightly above the temperature for which the specific volume is desired. It should also be noted that Joule's equivalent must be introduced, and appropriately chosen to correspond to the pressure and volume units, so that (43) will read

$$L = A T \frac{d p}{d t} (v_2 - v_1)$$

or solved for  $v_2$  and neglecting  $v_1$

$$v = \frac{L}{A T \frac{d p}{d t}} \quad \dots \quad (173')$$

From this equation,  $v$  is easily computed, and its reciprocal taken as the density.

**Entropy and Internal Heat of Fusion.**—These values are obtained, as in the case of vaporization, from (138) and (139), where  $L$  is the latent heat of fusion.

*Problem 71.*—Calculate the gain of entropy when one gramme of ice is melted at atmospheric pressure.

*Answer:* .2927.

*Problem 72.*—Calculate the loss of entropy when 10

grammes of mercury solidify at atmospheric pressure.

*Answer:* .01202.

*Problem 73.*—How much external work in joules is done, when one gramme of ice melts under a pressure of two atmospheres? (Consider the volumes as substantially the same as under one atmosphere, and take the density of water at  $0^{\circ}$  as .999868.) *Answer:* .01856 joules.

*Problem 74.*—What was the change in intrinsic energy in the preceding case, assuming that  $L$  is substantially the same as under atmospheric pressure? *Answer:* 79.904 calories.

**The Effect of Pressure on Fusion and Vaporization.**—The change of the temperature of fusion due to increased pressure may be computed with considerable accuracy by the equation of Clapeyron. In this case it is justifiable to write  $\frac{d p}{d t} = \frac{\Delta p}{\Delta t}$ , where the change of pressure may be taken almost as great as we wish. Solving for  $\Delta T$ , we have, from equation (43),  $\Delta T = \frac{A T}{L} \Delta p \Delta v$ , in which  $\Delta v$  is the change in volume due to the change of state,  $\Delta p$  the assumed change of pressure, and  $L$  is supposed known from experimental data.  $T$  should really be taken as the average of the range  $\Delta T$ , but considering that  $\Delta T$  is always very small, it is sufficient to take the initial temperature for an approximate solution. The raising of the temperature of vaporization by pressure can be found with precision, only if the pressure-temperature relations of the saturated vapor are known, as in the case of water. It could also be calculated by Clapeyron's equation, but that supposes a

knowledge of  $\Delta v$  and  $L$  at the temperature assumed, and therefore introduces more uncertainty than the more direct method.

*Problem 75.*—Calculate the lowering of the melting point of ice when it is subjected to a pressure of 60 atmospheres. *Answer:*  $-.447^{\circ}\text{C}$ .

### MIXTURES OF LIQUID AND VAPOR

The preceding cases become more complicated when vaporization is incomplete, but as the presence of a mixture of two phases is more common than a single phase, it is most important to be able to compute the various quantities involved in such mixtures.

**Specific Heat of Saturated Steam.**—In calculations of this kind, the specific heat  $c'$  at any assigned temperature is a valuable quantity to determine. It is easy to compute an approximate value, by combining (148) with Regnault's formula for  $H$  (142), from which we subtract  $ct$ , assuming  $c$  to be constant, as was done in deriving (143). Then  $L = 606.5 + .305t - ct$ , or in Fahrenheit  $L = 1091.7 + (.305 - c)(t - 32)$ . Differentiating with respect to  $t$ , and substituting in (148), we have

$$c' = .305 - \frac{L}{T}, \quad . \quad . \quad . \quad (174)$$

by which  $c'$  may be computed at any desired temperature. Although we have just assumed  $c$  as constant, it is desirable, in using formulæ where the product  $ct$  or  $\int c dt$  appears, to look up its value under "heat of the liquid" in the tables, rather than simply to set  $c = 1$ .

**Total Heat and Dryness of the Mixture.**—These quantities might be found by integrating (144), but it should be observed that  $c'$  is a function of  $T$ , and the form of this function, as derived in the last paragraph, can only be regarded as a good approximation. It is better, therefore, simply to take the values of  $L$  and  $c t$  from the tables, and if  $x$  is known, we have obviously  $q = L x + c t$ , or

$$x = \frac{q - c t}{L} \quad . \quad . \quad . \quad . \quad . \quad (175)$$

It is thus easy to calculate the dryness if the total heat and temperature of the mixture are given. Finally, a combination of (145) and (175) makes it possible to calculate the total heat of a mixture, when only the temperature and specific volume are given.

**Problem 76.**—Calculate the specific heat of saturated steam, under a pressure of 1488.9 mm. of mercury.  
*Answer:*  $-1.032$ .

**Problem 77.**—What is the total heat of a mixture of 60 grammes of water and steam at  $135^{\circ}$  C., when 12 grammes are evaporated? *Answer:* 1432.5 calories.

**Problem 78.**—Calculate the dryness of a mixture of 3 lbs. of water and steam whose total heat is 2,100 B.T.U., at a temperature of  $320^{\circ}$  F. *Answer:* 45.8 per cent.

**Problem 79.**—A mixture of 20 grammes of water and steam occupy 3 litres at a temperature of  $140^{\circ}$  C. Find  $x$  by (145). *Answer:* 29.4 per cent.

**Problem 80.**—A mixture of 3 lbs. of water and steam occupy 2 cubic feet, at a temperature of  $330^{\circ}$  F. Find the total heat of the mixture. *Answer:* 434.8 B.T.U.

**Change of Entropy of the Mixture.**—When passing from one degree of dryness to another at constant tem-

perature, the change of entropy is obtained by (152), or

$$S_1 - S_2 = \frac{L(x_1 - x_2)}{T}.$$

But when the temperature changes as well, we may make the computation by (151)

$$S_1 - S_2 = \frac{L_1 x_1}{T_1} - \frac{L_2 x_2}{T_2} + c \log \frac{T_1}{T_2}$$

(NOTE.—The entropy of vaporization  $\frac{L}{T}$ , as well as the entropy of the liquid above  $t_o$ , or  $\int_{t_o}^{t_c} \frac{dt}{t}$ , are given in the tables.)

*Problem 81.*—Calculate the difference in entropy between one kg. of a mixture of steam and water when  $x = .24$  at  $135^\circ$  C., and  $x = .1$  at  $160^\circ$  C. *Answer:* .1274.

*Problem 82.*—Six pounds of a mixture of steam and water are enclosed in a receiver of 25 cu. ft. capacity, at a temperature of  $260^\circ$  F. What is the gain in entropy when the receiver is heated to  $320^\circ$  F.? *Answer:* 3.55.

*Problem 83.*—Calculate the change of entropy in the last problem, if the volume were increased to 40 cu. ft., without change of temperature. *Answer:* 1.665.

**Change of Dryness During Adiabatic Expansion.**—From a practical standpoint, it is frequently desirable to calculate the changing proportions of liquid and vapor during expansion in the cylinder of an engine. The determination of the value of  $x$ , after an adiabatic expansion to some given temperature, from a given initial dryness and temperature, is effected by equation (153), which is commonly used in the study of cylinder condensation. The application of this equation to steam is perfectly simple, since it is only necessary to find  $L_1$  and  $L_2$  in the



tables, corresponding to  $T_1$  and  $T_2$ , which are supposed to be given either directly, or through a knowledge of the pressures.

*Problem 84.*—The initial dryness of a mixture of water and steam is .7 at a temperature of  $360^\circ$  F. What is the final dryness, if adiabatic expansion is carried down to one atmosphere? *Answer:* 64.77 per cent.

*Problem 85.*—The initial dryness of a mixture of water and steam is .9, under a pressure of 9404 mm. of mercury; find  $x_2$  after adiabatic expansion to a temperature of  $120^\circ$  C. *Answer:* 80.91 per cent.

Equation (153) may also be used to calculate the final dryness, or the final volume, if the initial volume is given; for  $x$  may be found from (145) when  $v$  is given,  $v''$  is known from  $T$ , and  $v'$  is practically unity, or .001 litres per gramme, or 62.4 cu. ft. per lb., according to the units chosen. The same equation may also be used to calculate the mass of the mixture. If the total volume, dryness, and temperature (consequently  $v''$ ), are known,

we may write  $x = \frac{\frac{V}{m} - v'}{v'' - v'}$  where everything is given

but  $m$ . In many actual cases only the final volume of an adiabatic expansion is known. To facilitate the determination of both final dryness and temperature, tables have been prepared, such as Peabody's, in which the specific volume of the mixture, as well as the dryness are given for each degree of temperature, under an ascending series of entropy values. Thus if  $v_1$  and  $T_1$  are known for the mixture, we readily find the value of  $s_1$  corresponding to that particular combination of water and steam. Then if  $s$  is supposed to be constant, we have

only to enter the table under that entropy value and find  $T_2$  and  $x_2$  corresponding to  $v_2$ .

*Problem 86.*—Four lbs. of a mixture occupy 10 cubic feet at  $371^\circ$  F. Adiabatic expansion occurs to 32 cu. ft. What are  $T_2$  and  $x_2$ ? *Answer:*  $T_2 = 277^\circ$ ,  $x_2 = .886$ .

*Problem 87.*—Eighteen grammes of a mixture of steam and water occupy 3 litres at a temperature of  $170^\circ$  C. What is the dryness if the pressure falls adiabatically to 3 atmospheres? *Answer:* 69.27 per cent.

*Problem 88.*—Three cubic feet of a mixture of water and steam are 60 per cent dry at a temperature of  $300^\circ$  F. What is the total volume after adiabatic expansion to a pressure of 30 lbs. per sq. inch? *Answer:* 6.27 cu. ft.

**Entropy and Intrinsic Energy of the Mixture.**—The entropy is obtained, in the case of water, from (152'), which is simply the sum of the entropy of the liquid above the freezing point, which is given in the tables, and that of evaporation. The gain in intrinsic energy is to be found by using (155), in which  $v'$  is practically unity;  $L$ ,  $v''$  and  $p_1$  may be found from the tables if  $T$  is given, and  $x_1$  must be known directly or indirectly, and the second term must be multiplied by  $A$ .

*Problem 89.*—Calculate the entropy above  $0^\circ$  C. of 24 kg. of steam and water which occupy 5 cubic metres at a temperature of  $165^\circ$ . *Answer:* 32.1 kg. cal./ $T$ .

*Problem 90.*—Calculate the intrinsic energy above  $32^\circ$  F. of a mixture of water and steam, which occupy 10 cubic feet, when  $x = .7$ , under a pressure of 70 lbs. per sq. in. *Answer:* 1960 B.T.U.

## ENERGETICS OF MIXTURES OF WATER AND STEAM

**Adiabatic Expansion.**—The most satisfactory method for calculating the external work, when steam expands adiabatically, is to use equation (162) in which  $\rho_1$  and  $\rho_2$  are to be found in the tables under “heat equivalent of internal work.” The integral,  $\int_{T_2}^{T_1} c dT$ , is the difference between the heats of the liquid at the two given temperatures, and is also found in the tables;  $x_1$  must be known, or may be calculated directly from the data, and  $x_2$  is found by using equation (153).

*Problem 91.*—How much work is done by the adiabatic expansion of 2 kg. of a mixture of steam and water from  $200^\circ \text{C.}$ , and  $x = .6$ , to a final temperature of  $150^\circ \text{C.}$ ?  
*Answer:* 175,400 joules.

*Problem 92.*—How much work is done when 60 grammes of a mixture of water and steam change adiabatically from a volume of 8 litres at  $150^\circ \text{C.}$ , to a pressure of one atmosphere? *Answer:* — 1529. joules.

*Problem 93.*—If a mixture of water and steam occupy 3 cu. ft., under a pressure of 80 lbs. per sq. in., and a dryness of .95, calculate the work done by an adiabatic expansion which doubles the volume.

(NOTE.—Use temperature-entropy tables to find  $T_2$  and  $x_2$ .) *Answer:* 23,430 ft.-lbs.

**Isothermal Expansion.**—The work done by an isothermal expansion (or expansion under constant pressure) is easily computed by (163), where, as was explained,  $x_1$ ,  $x_2$  and  $T$  are given either directly or indirectly.

*Problem 94.*—Calculate the work done by 2 lbs. of a mixture of water and steam which occupy 2 cubic feet,

and expand isothermally at  $280^{\circ}\text{F.}$ , to a final volume of 5 cubic feet. *Answer:* 21,280 ft.-lbs.

*Problem 95.*—Calculate the work done by 12 cu. ft. of a mixture of water and steam whose dryness is .45, under a pressure of 75 lbs. per sq. in., if it expands till all the water is vaporized. *Answer:* 157,900 ft.-lbs.

**Isoenergetic Expansion.**—If  $u$  remains constant, we may use equation (161) to calculate the work done, where the exponent  $\nu$  is substituted for  $\mu$  in the denominator, and  $\nu$  is calculated by (164). To apply (164) we must know  $p_1$ ,  $v_1$  and  $p_2$  either directly or indirectly;  $x_2$  is found by setting  $\Delta u = 0$  in (162), thus adapting it to isoenergetic expansion; and  $v_2$  is easily calculated if  $x_2$  is known.

*Problem 96.*—Calculate the work done when 40 grammes of a mixture of water and steam, whose dryness is .5, expand isoenergetically from a pressure of 7010 mm. of mercury, to one of 3030.5 mm. *Answer:* 338. joules.

**Expansion of Dry Saturated Steam.**—If the expanding vapor is jacketed so as to just keep it dry and saturated during the expansion, then equation (165) is to be used. The values of  $a$  and  $b$  may be found from equation (143) by setting  $t = (T - 273)$ ; hence

$$L = 796.2 - .695 T, \text{ or in Fahrenheit,}$$

$$L = 1433.6 - .695 T.$$

It is then only necessary to know the initial and final temperatures, and these can always be found, if the pressures, or specific volumes are given. The right-hand member must, of course, be multiplied by  $J$  to reduce it to mechanical units.

*Problem 97.*—What is the work done by 2.5 lbs. of

dry saturated steam expanding from a volume of 8 cu. ft. to a final pressure of one atmosphere? *Answer:* 341,700 ft.-lbs.

**General "Exponential Expansion."**—The preceding method may be used for the general case of any expansion which approximately follows an exponential curve of the form  $p v^n = K$ . This method is well adapted to curves that lie between the adiabatic and isothermal, and that cannot be treated by either of the methods already explained. In such cases  $n$  is found by (164), like  $\nu$ , and the work done follows from any of the equations based upon a similar type of expansion, whether derived under the head of perfect gases where the exponent was  $\kappa$ , or the adiabatic expansion of saturated steam, where the exponent was  $\mu$ . In a problem of this kind, it is necessary to know both the initial and final pressures and specific volumes, either directly or indirectly, therefore (161) is a suitable one to calculate the work.

*Problem 98.*—Calculate the work done, when 8 kg. of a mixture of steam and water expand from  $p_1 = 10$  atmospheres, and  $V_1 = .9$  cu. metres, to  $p_2 = 4$  atmospheres and  $V_2 = 2.8$  cu. metres. *Answer:* 1,998,000 joules.

**Closed Cycles.**—In case the expanding mixture performs a complete cycle of operations, the work done depends upon the particular cycle used. Those considered in the text are the Carnot, Clausius, and the non-expansion cycles; and the work done in each case is readily computed by (166), (166'), and (167). In the case of the Carnot cycle,  $T_2$  may be found if  $p_3$  or  $v_3$  are given, while  $x_1$  and  $x_2$  may be made to depend upon the initial and final volumes of the isothermal expansion.

*Problem 99.*—A mixture of 10 lbs. of water and steam

perform a Carnot cycle where the following data are given:  $T_1 = 340^\circ \text{ F.}$ ,  $V_1 = 15 \text{ cu. ft.}$ ,  $V_2 = 36 \text{ cu. ft.}$ , and  $p_3 = 20 \text{ lbs. per sq. in.}$  How much work is performed in one cycle? *Answer:* 53,290 ft.-lbs.

*Problem 100.*—Twelve kilogrammes of water are passed through a Clausius cycle, where  $T_1 = 165^\circ \text{ C.}$ , and  $T_2 = 100^\circ \text{ C.}$ ; calculate the work done and the efficiency, and compare the latter with that of a Carnot cycle between the same temperature limits. *Answer:* 3,998,000 joules. 14.2 per cent.

*Problem 101.*—How much work is done by 2 lbs. of dry saturated steam which act in a non-expansion *condensing* cycle where  $T_1 = 280^\circ \text{ F.}$ , and  $p_2 = 2 \text{ lbs. per sq. inch?}$  *Answer:* 117,200 ft.-lbs.

**Sublimation Pressure.**—Kirchoff's formula (168) may be reduced to a form adaptable to numerical calculation. The first term of the left-hand member equals  $\frac{L_1}{T_p}$ , or more properly  $\frac{J L_1}{T_p}$ , and if we consider  $v_1$  and  $v_2$  as negligibly small compared to  $v_3$ , the equation reduces to  $\frac{J L_1}{T_p} + v_3 \frac{d p_2}{d T} = v_3 \frac{d p_3}{d T}$ ; or, taking finite increments  $\frac{\Delta p}{\Delta T} = \frac{J L}{T v_3}$ , and in terms of the notation of Fig. 40, where  $a b = \Delta p_1 - \Delta p_2$ .

$$\frac{a b}{T_p - T_1} = \frac{J L_1}{T_p v_3} \quad . \quad . \quad . \quad (176)$$

This enables us to calculate the sublimation curve from the vaporization curve produced, or, in other words, the vapor pressure of the solid at temperatures below the triple point.

*Problem 102.*—In the case of water  $L_1 = 79.9$ ,  $T_p = 273.0076^\circ$ ,  $v_3$  is about 206 litres per gramme. Calculate the difference of pressure  $a b$  between the vaporization and sublimation curves at a temperature two degrees below the triple point. *Answer:* 119. dynes/cm.<sup>2</sup>.





TABLE I  
FACTORS FOR CONVERSION OF ENERGY UNITS

	Gramme-Calories	B. T. U.	Joules	Foot-Pounds	Kilogr.-Metres	Litre-Atmos.	Cu.-Ft.-Atmos.	Foot-Poundals	Horse-Pow. Hours
Gramme-Calorie	1	$3.968 \times 10^{-3}$	4.185	3.087	.4267	$4.130 \times 10^{-2}$	$1.459 \times 10^{-3}$	99.31	$1.5591 \times 10^{-6}$
B. T. U.	252	1	1055	777.9	107.5	10.41	.3676	25030	$3.929 \times 10^{-4}$
Joule	.2389	$9.482 \times 10^{-4}$	1	.73756	.1019	$9.869 \times 10^{-3}$	$3.485 \times 10^{-4}$	23.73	$3.725 \times 10^{-7}$
Foot-Pound	.3240	$1.286 \times 10^{-3}$	1.356	1	.13826	$1.3381 \times 10^{-2}$	$4.7253 \times 10^{-4}$	32.174	$5.0505 \times 10^{-7}$
Kilogr.-Metre	2.343	$9.298 \times 10^{-3}$	9.806	7.2327	1	$9.678 \times 10^{-2}$	$3.4177 \times 10^{-3}$	232.7	$3.6529 \times 10^{-6}$
Litre-Atmos.	24.21	$9.607 \times 10^{-2}$	101.32	74.733	10.333	1	$3.5319 \times 10^{-2}$	2403.8	$3.7734 \times 10^{-5}$

TABLE II  
PERFECT GAS CONSTANT  $R$  PER GRAMME MOLECULE AND POUND MOLECULE

Pressure Expressed in ↓	Volume Expressed in —	Cubic Centimetres	Litres	Cubic Metres	Cubic Inches	Cubic Feet
Dynes per Sq. Centimetre	$R$ , per gramme-molecule =	$8.317 \times 10^7$	$8.317 \times 10^4$	$8.317 \times 10$		
Kilogrammes per Square Metre	$R$ , per gramme-molecule =	$8.48 \times 10^5$	$8.48 \times 10^2$	$8.48 \times 10^{-1}$		
Atmospheres	$R$ , per gramme-molecule =	$8.209 \times 10$	$8.209 \times 10^{-2}$	$8.209 \times 10^{-5}$		
Pounds per Square Inch	$R$ , per pound-molecule =				18510	10.71
Pounds per Square Foot	$R$ , per pound-molecule =				$2.666 \times 10^6$	1543
Atmospheres	$R$ , per pound-molecule =				1260	.7289

(For air,  $R = 29.20$  Kg.-Metres per kilogramme, or 53.18 Ft.-lbs. per lb.)

TABLE III  
DENSITY, SPECIFIC HEAT, AND MOLECULAR WEIGHT OF CERTAIN GASES  
(Density and Specific Volume are at 0° C., and Standard Atmosphere)

Gas	Density gr./litre	Density lbs./cu. ft. $\times 10^{-2}$	Density Air = 1	Specific Volume litres/gr.	Specific Heat at constant $p$ .	Ratio of Specific hts. $K$	Molecular Weight
Air	1.2928	$8.0708 \times 10^{-2}$	1	.77352	0° to 200° .2375	1.4029	29 effective
CO <sub>2</sub>	1.9652	.12269	1.529	.50885	11° to 214° .2169	1.291	44
H <sub>2</sub>	$9.004 \times 10^{-2}$	$5.621 \times 10^{-3}$	$6.9 \times 10^{-2}$	11.106	12° to 198° 3.409	1.41	2.016
N <sub>2</sub>	1.2542	$7.83 \times 10^{-2}$	.97	.79732	0° to 200° .2438	1.41	28.08
O <sub>2</sub>	1.4292	$8.9233 \times 10^{-2}$	1.105	.69969	13° to 207° .2175	1.41	32
NH <sub>3</sub>	.7621	$4.7577 \times 10^{-2}$	.59	1.3122	27° to 200° .5356	1.28	17.06

(To reduce density in grammes per litre to lbs. per cu. ft., divide by 16.018.)

TABLE IV  
THERMOMETRIC AND CALORIMETRIC CONSTANTS OF CERTAIN SUBSTANCES  
(Temperatures are Centigrade; heat in gramme-calories per gramme)

Name of Substance	Melting Point	Boiling Point	Heat of Fusion	Heat of Vaporization	Specific Heat of Solid (Aver. Value)	Specific Heat of Liquid	Specific Heat of Gas at Constant $p$
Water	0°	100°	79.9	536	.505	at 15° 1	at 100° .4
Alcohol	- 112.3°	78.4°				at 20° .602	.4534
Ammonia	- 75°	- 38.5°	108.1	295		at 20° 1.190	.53
Ether	- 117.6°	35°		90		at 30° .547	.43
Carbon Bisulphide	- 110°	46.2°		87		at 30° .24	.1596
Mercury	- 38.3°	357°	2.82	62	3.19 $\times 10^{-2}$	(average) 3.3 $\times 10^{-2}$	

TABLE IV—*Continued*  
 THERMOMETRIC AND CALORIMETRIC CONSTANTS OF CERTAIN SUBSTANCES  
 (Temperatures are Centigrade; heat in gramme-calories per gramme)

Name of Substance	Melting Point	Boiling Point	Heat of Fusion	Heat of Vaporization	Specific Heat of Solid (Aver. Value)	Specific Heat of Liquid (Aver. Value)	Specific Heat of Gas at Constant $p$
Lead	326°	1450° to 1600°	5.37		$3.1 \times 10^{-2}$	$4.1 \times 10^{-2}$	
Zinc	419°	918°	28		$9.3 \times 10^{-2}$		
Copper	1083°	2100°	43		$9.4 \times 10^{-2}$		
Air				44 to 51.7			.2375
Oxygen		— 188°		59		.347	.2175
Nitrogen				49.83		.43	.2438

TABLE V  
DENSITY AND THERMO-ELASTIC COEFFICIENTS OF CERTAIN LIQUIDS AND SOLIDS  
(Compressibility in atmospheres; Young's Modulus in Kg. per sq. Metre; temperature in degrees Centigrade)

Name of Substance	Density $\rho$	Coefficient of Expansion $\alpha_p$	Compressibility $\gamma_T = \frac{1}{E_T}$	Young's Modulus
Water	(at 20°) .998230	(4°-100°) $4.3 \times 10^{-4}$	(1-25 atmos. and 20°) $4.91 \times 10^{-5}$	
Alcohol	(at 15°) .7937	(0°-30°) $1.101 \times 10^{-3}$	(one atmos. and 20°) $1.01 \times 10^{-4}$	
Glycerine	(at 20°) 1.2604	(at 20°) $5.05 \times 10^{-4}$	$25.1 \times 10^{-6}$	
Ether	(at 4°) .7313	(0°-30°) $1.617 \times 10^{-3}$	(8-25 atmos. and 25°) $1.69 \times 10^{-4}$	
Carbon Bisulphide	(at 20°) 1.264	(0°-30°) $1.197 \times 10^{-3}$	(8-35 at. and 15.6°) $8.7 \times 10^{-5}$	
Mercury	(at 20°) 13.546	(0°-100°) $1.809 \times 10^{-4}$	(one atmos. and 0°) $3.92 \times 10^{-6}$	

TABLE V—*Continued*

DENSITY AND THERMO-ELASTIC COEFFICIENTS OF CERTAIN LIQUIDS AND SOLIDS  
(Compressibility in Atmospheres; Young's Modulus in Kg. per sq. Metre; temperature in degrees Centigrade)

Name of Substance	Density $\rho$	Coefficient of Expansion $\alpha$	Compressibility $\gamma = \frac{1}{E_T}$	Young's Modulus
Lead (Cast)	(at 0°) 11.37	(0°-100°) $2.799 \times 10^{-5}$ (linear expansion)		(at 15°) 1803 (drawn)
Zinc (Cast)	7.1 (average)	(at 50°) $2.9 \times 10^{-5}$ (linear expansion)		(at 15°) 8734 (drawn)
Copper (Cast)	8.6 (average)	(0°-100°) $1.718 \times 10^{-5}$ (linear expansion)		(at 15°) 12450 (drawn)
Ice	(at 0°) .916	$2.37 \times 10^{-5}$ (linear expansion)		276

TABLE VI  
CRITICAL AND VAN DER WAALS CONSTANTS

(Pressure in atmospheres;  $a$  and  $b$  in terms of atmosphere and normal specific volume as units;  
temperature Centigrade)

Substance	$t_c$	$p_c$	$a$	$b$	Observer
Water	365°	200.5	.01149	.001457	Cailletet and Colardeau
Alcohol	243.6°	62.76	.02407	.003769	Ramsay and Young
Ammonia	130°	115	.00798	.001606	Dewar
Ether	194.4°	35.61	.03473	.006011	Young
CS <sub>2</sub>	275°	77.8	.02185	.003225	Cagniard de la Tour
CO <sub>2</sub>	31.9°	77	.00683	.001813	Dewar
H <sub>2</sub>	-234.5°	20	.00042	.000881	Olszewski
N <sub>2</sub>	-146	34	.00259	.001655	von Wroblewski
O <sub>2</sub>	-118	50	.00273	.001419	von Wroblewski



TABLE VI—*Continued*Critical Volumes in Terms of  $v_0$ 

Water	.003864	Battelli	
Alcohol	.00713	Dewar	
Ether	.01584	Battelli	
CO <sub>2</sub>	.0066	Andrews	

TABLE VII

COEFFICIENTS OF EXPANSION OF GASES

 $\alpha_p$  between 0° and 100°

Substance	1 Atmosphere	100 Atmospheres	200 Atmospheres	500 Atmospheres	1000 Atmospheres
Air	.00367	.00444	.00455	.00331	.00214
H <sub>2</sub>	.00366		.00332	.00278	.00218
CO <sub>2</sub>	.00371	.0414	.0111	.00349	.00206

 $\alpha_v$  Atmospheres

Substance	1	50	100	200	500
Air	.00366	.00371	.00462	.00552	.00617
H <sub>2</sub>	.00367		.00373	.00383	.00379
CO <sub>2</sub>	.00369	.00386	.00373		

TABLE VIII  
CONVERSION OF PRESSURE UNITS

Unit	Dynes per Square Centimetre	Gr. per Sq. Cm.	Kilo. per Sq. Metre	Mm. of Mercury	Atmos- pheres	Lbs. per Sq. Inch	Lbs. per Sq. Foot.
Dyne per Square Centimetre	1	$1.0198 \times 10^{-3}$	$1.0198 \times 10^{-2}$	$7.5010 \times 10^{-4}$	$9.8697 \times 10^{-7}$	$1.4505 \times 10^{-5}$	$2.0887 \times 10^{-3}$
Gramme per Square Centimetre	980.6	1	10	$7.3551 \times 10^{-1}$	$9.6777 \times 10^{-4}$	$1.4223 \times 10^{-2}$	2.0481
Kilogramme per Square Metre	98.06	$10^{-1}$	1	$7.3551 \times 10^{-2}$	$9.6777 \times 10^{-5}$	$1.4223 \times 10^{-3}$	$2.0481 \times 10^{-1}$
Millimetre of Mercury	1333.2	1.3595	13.595	1	$1.3158 \times 10^{-3}$	$1.9337 \times 10^{-2}$	2.7845
Atmosphere	1,013,200	1033.3	10333	760	1	14.696	2116.32
Pound per Square Inch	68944	70.308	703.12	51.715	$6.8046 \times 10^{-2}$	1	144
Pound per Square Foot	478.78	$4.8825 \times 10^{-1}$	4.8828	$3.5912 \times 10^{-1}$	$4.7252 \times 10^{-4}$	$6.9445 \times 10^{-3}$	1

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